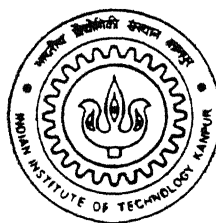# ROLE OF MANGANESE IN DESULPHURIZATION OF BLAST FURNACE METAL

by

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INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

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ROLE OF MANGANESE IN DESULPHURIZATION OF ,BLAST FURNACE METAL

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by

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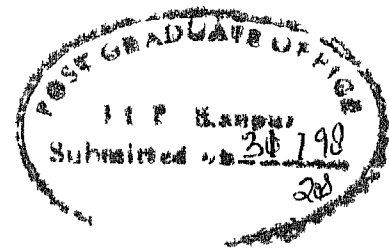
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CERTIFICATE

It is certified that the work contained in this thesis entitled *"Role of Manganese in desulphurization of Blast Furnace metal "*, by *Alok Dobriyal*, has been carried out under my supervision and that this work has not been submitted elsewhere for any degree

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Kanpur [July, 1998]

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Abstract

Model equations have been developed and solved using a computer to predict sulphur content of blast furnace iron with addition of manganese and iron sulphide One silicon carbon furnace capable to reach 1400°C was designed and fabricated in the laboratory for doing experiment in the present study Some experiments were carried out in the molybdenum disilicide raising hearth furnace at 1500°C Results of experiment show that sulphur content decreases with an increase in manganese content of hot metal Measured values of sulphur do not match the predicted values at 1500°C but agree well with predicted values in the temperature range of 1200 to 1300°C Considerable drop in sulphur occurs during cooling stages

Measured sulphur content at fixed manganese additions and with no slag addition decreases with a decrease in temperature Results of the experiments match with predicted values using the model equations Additions of lime bearing slag does not effect much the manganese-sulphur relation at any temperature

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Chapter 1

INTRODUCTION

Presence of sulphur in steel is considered harmful as it lowers the mechanical properties of the steel. Low sulphur in steel is essential for getting improved notch toughness, ductlity and cold pressing properties etc. and to avoid problems such as cracking and directional anisotropy encountered during hot working. If sulphur content is high, sulphur in steel gives rise to lamellar tearing in weld joints. For production of quality steel for special applications, sulphur in steel should be less than 0.01 percent. For general purpose sulphur in steel may be in the range of 0.02 to 0.05 percent.

Main source of sulphur in steel is the blast furnace melt. Sulphur is carried into the blast furnace via raw materials in the form of iron sulphide, calcium sulphide and organic sulphides. The amount of sulphur brought in by the ore and the flux is much less compared to that brought in by the coke. Depending upon the origin, the ore and coke may contain sulphur ranging from 0.05 to 0.1 percent and 0.6 to 1.5 percent respectively. In a blast furnace, most of the sulphur is removed in the slag. Typical sulphur balance per ton of hot metal produced by the blast furnace is represented in Table 1.1.

Control of sulphur in steel should be done in the blast furnace stage itself as the extent of sulphur removal in steel making is small. Factors that control the sulphur content in the blast furnace iron include the coke rate, sulphur content of coke, slag volume and sulphur distribution ratio (α). Ignoring sulphur input via ore and fluxes and sulphur in flue gases, sulphur balance gives the following.

Table 1 1   Typical furnace sulphur balance in blast furnace for one ton of metal

Material	sulphur input		sulphur output	
	kg	%	kg	%
coke(%S) 600kg/THM	60	80		
Charge materials	1 5	20		
Iron(0 03%S)			0 3	4
Flue and dust gas			0 37	5
slag			6 82	91
Total	7 5		7 5	

$$[wt\%S] = \frac{(wt\%S)_{coke} * cokerate}{1000 + \alpha * W_{sl}} \qquad (1\ 1)$$

where α is the sulphur partition ratio which is defined as follows

$$\alpha = \frac{(\%S)_{slag}}{[\%S]} \qquad (1\ 2)$$

$[wt\%S]$ is the percentage of sulphur in hot metal, $(wt\%S)_{slag}$ percentage of the sulphur in the slag and W_{sl} is the amount of slag produced per ton of hot metal Since the slag rate should be kept low for other advantages and coke rate can not be changed appreciably, low sulphur can be achieved only at high sulphur distribution ratio High sulphur distribution ratio can be obtained by maintaining high slag basicity, high metal temperature and low Feo content of the slag

In some cases, techno economic consideration may not justify removal of sulphur to low level either in blast furnace or in steel making So resort is being made to a great extent to remove sulphur outside the blast furnace The practice is known as external desulphurization of the hot metal

1 1   Scope of present work

The present work involved the studies on manganese sulphur interaction in the blast furnace metal Attempts are made to simulate conditions existing in a blast furnace as to show extent of sulphur removal with the addition of manganese with and without addition of slag of different basicity The work involved designing and setting up of arrangements in the laboratory for studying the reactions Theoretical calculations are made to study thermodynamics of the reactions

Chapter 2

LITERATURE REVIEW

One of the important functions of blast furnace is control of sulphur to low levels in the hot metal before it is refined in the steel making furnace. Lot of scientific investigation on desulphurization has been done to study the slag-metal and metal-slag-gas equilibria within the blast furnace and outside the blast furnace. A comprehensive literature survey is presented in this chapter

2 1 Activity of sulphur in liquid iron alloy

Systematic work on the distribution of sulphur between slag and metal by first finding the activity of sulphur in liquid iron base alloy was carried out by Sherman and Chipman (1)

2 1 1 Experimental approach to determination of thermodynamic data

The experiments designed to study sulphur activity were based on attainment of equilibrium between sulphur in the melt and gaseous atmosphere containing hydrogen and hydrogen sulphide The reaction can be written as below;

$$[S] + H_2(g) = H_2S(g) \tag{2 1}$$

$$K_1 = \frac{P_{H_2S}}{P_{H_2} a_S} \tag{2 2}$$

The standard free energy of equation (2 1) can be written as

$$\Delta G^o = -RT ln K_1 \tag{2 3}$$

Equation (2 2) in the modified form can be rewritten as

$$K_2 = \frac{P_{H_2S}}{P_{H_2} f_S[wt\%S]} \tag{2 4}$$

where P_{H_2S} and P_{H_2} are the partial pressure of H_2S and H_2 respectively in the gaseous mixture and a_s represent the activity of sulphur in the melt

$$a_S = f_S[wt\%S] \tag{2 5}$$

where f_S = activity coefficient of sulphur in liquid iron

$[wt\%s]$ = percentage of sulphur in the melt

In a multicomponent system containing N solutes, f_S is given by the following equation

$$\log f_S = \sum_{j=1}^{N} e_S^j \, wt[\%j] \tag{2 6}$$

c_S^j is the henrian activity interaction parameter for $1 wt\%$ standard state It gives effect of solute j on the activity coefficient and is defined as

$$e_S^j = \left(\frac{\partial \log f_S}{\partial wt\%i}\right)_{wt\%Fe \to 100} \tag{2 7}$$

As the concentration of solute tends to zero equation, (2 4) get modified as

$$K_2 = \left[\frac{P_{H_2S}}{P_{H_2} * [wt\%S]}\right](\%wtS) \to 0 \tag{2 8}$$

From the results of experiments of equilibriating the iron melt with certain H_2S and H_2 ratio and finding the corresponding equilibrium sulphur content of the metal, one can determine the following ratio

$$K_3 = \left[\frac{P_{H_2S}}{P_{H_2} * [wt\%S]}\right] \tag{2 9}$$

A typical plot of $(\log K_3)$ vs $[\%S]$ is shown in Fig 2 1 Value of K_2 was obtained by extra-plotting the plot to zero percent sulphur Then for any finite concenteration activity coefficient of the sulphur was determined by using equation 2 4

2 1 2 Iron - Sulphur system

Standard free energy of formation of H_2S from gases such as H_2 and S_2 has been reported by Banya and Chipman (2) as follows

$$H_2(g) + 1/2S_2 = H_2S \qquad \Delta G^* = -21820 + 11\ 92T \quad cal \qquad (2\ 10)$$

Investigators calculated the standard free energy of formation of reaction (2 10) by finding the heat and entropy of formation and reported the following

$$\Delta G^0 = -21530 + 11\ 37T \quad cal \qquad (2\ 11)$$

They also investigated the effect of sulphur in liquid iron at 1600^oC by studying the gas - metal equilibrium and obtained the data below

$$H_2(g) + [S] = H_2S(g) \qquad \Delta G^o = 10750 + 6\ 13Tcal \qquad (2\ 12)$$
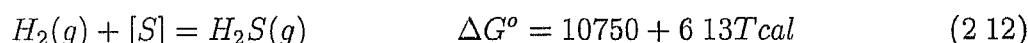
Combining (2 11) and (2 12) one may get

$$1/2S_2(g) = [S] \qquad \Delta G^o = -32280 + 5\ 60Tcal \qquad (2\ 13)$$

Activity coefficient f_S was reported to vary with sulphur content of iron at 1600^oC as follows

$$\log f_S = -0\ 0282[wt\%S] \qquad (2\ 14)$$

This gives value of interaction parameter as below

$$e_s^s = -0\ 0282 \qquad (2\ 15)$$

2 1 3 Iron - Carbon - Sulphur System

Carbon has pronounced effect on the activity of sulphur in the melt Morris and Bhel (3) studied the solubility of sulphur in the iron-carbon alloy by equilibrating the melt with
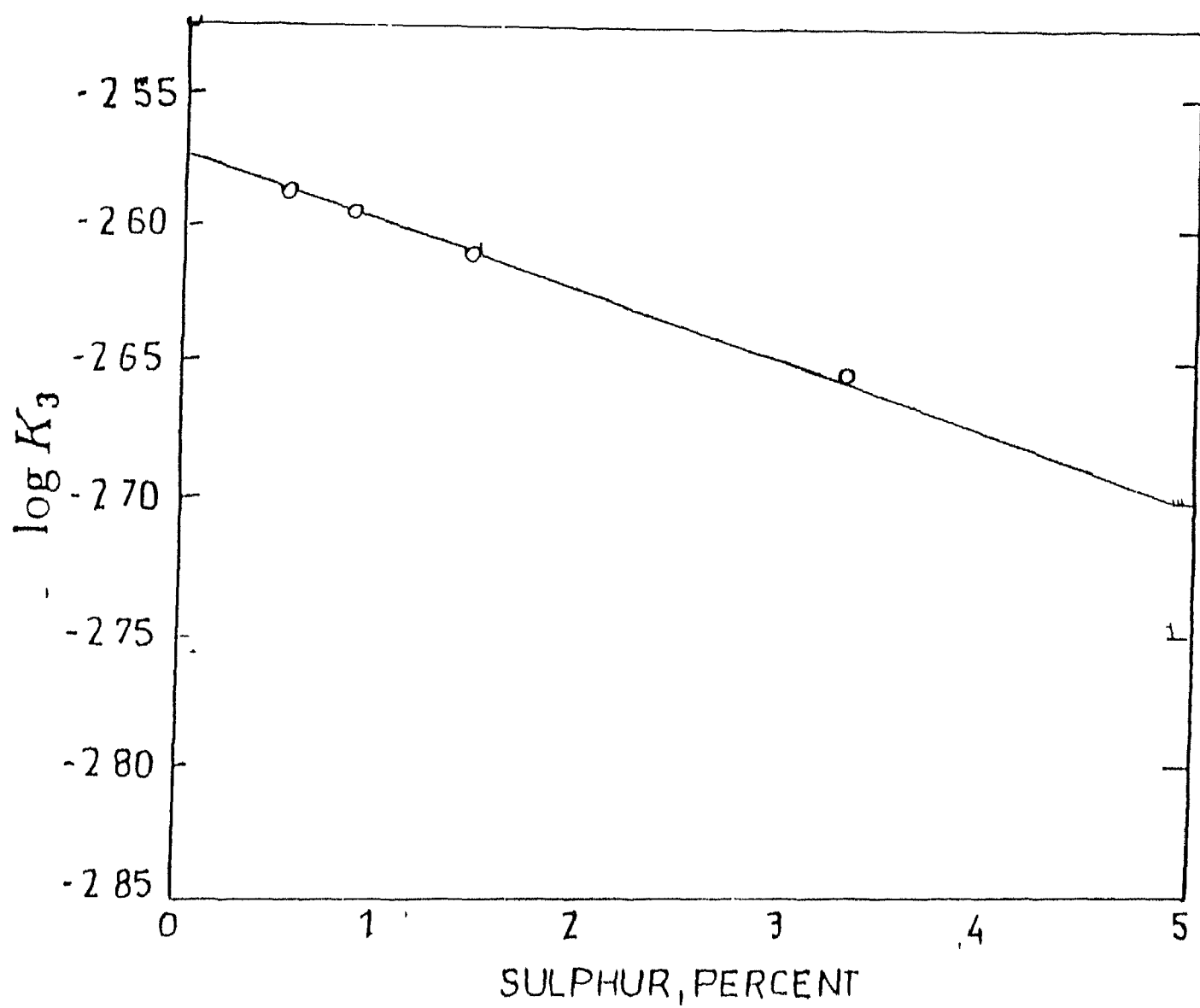
Figure 2 1   Effect of sulphur concentration on K_3

$H_2 - H_2S$ gas mixture Then results are given in Fig 2 2

From the figure it is clear that there is an increase in the activity of sulphur in the melt They found that the the interaction parameter, e_S^C (which is the slope of $\log f_S$ vs $wt\%C$) have a value of 0 12 in the concentration range of 1-2 wt pct carbon For carbon concentration beyond 2 pct, $\log f_s$ vs $[wt\%C]$ plot is nonlinear and equation 2 7 can not be applied directly to find e_c^s value The slope of $\log fs$ vs $[wt\%C]$ plot is around 0 24 when the carbon concentration was in the range of 4 to 5 wt pct This value is sometime taken as interaction parameter for the carbon saturated solutions

It was proposed by them that to find value of f_s accurately for a carbon saturated solution, it is desirable to use 4 35 pct carbon in iron as standard state The free energy for the new standard state is obtained as follows

$$1\ 2S_2(g) = S(4\ 34\%C) \qquad\qquad \Delta G^o = -23,880 + 3\ 90Tcal \qquad\qquad (2\ 16)$$
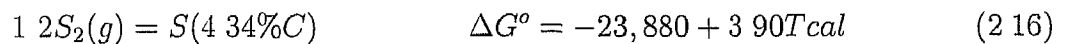
Equation (2 13) is related to equation(2 16) by the following relation

$$\Delta G_f^o(4\ 35) = \Delta G^o + RT ln f_s(4\ 35\%C) \qquad\qquad (2\ 17)$$

f_s value has been reported as 4 2 at 1600^oC for a carbon concentration of 4 35%, Since the slope of a carbon $\log fs$ vs$[wt\%C]$ plot is 0 24 at this carbon level, f_S at any other carbon level can be determined as follows

$$\log f_s^c = \log 4\ 2 + 0\ 24(X - 4\ 35) \qquad\qquad (2\ 18)$$

where , X - weight % carbon in the melt

2 1 4   Effect of alloying elements on activity of sulphur

Sherman and Chipman [1] studied activity of sulphur in the iron melt containing various elements like manganese , copper and silicon etc at 1600^oC They plotted $\log f_s$ vs $[wt\%i]$ (where i= may be any alloying element) curve From the curve e_i^S, can be calculated in each
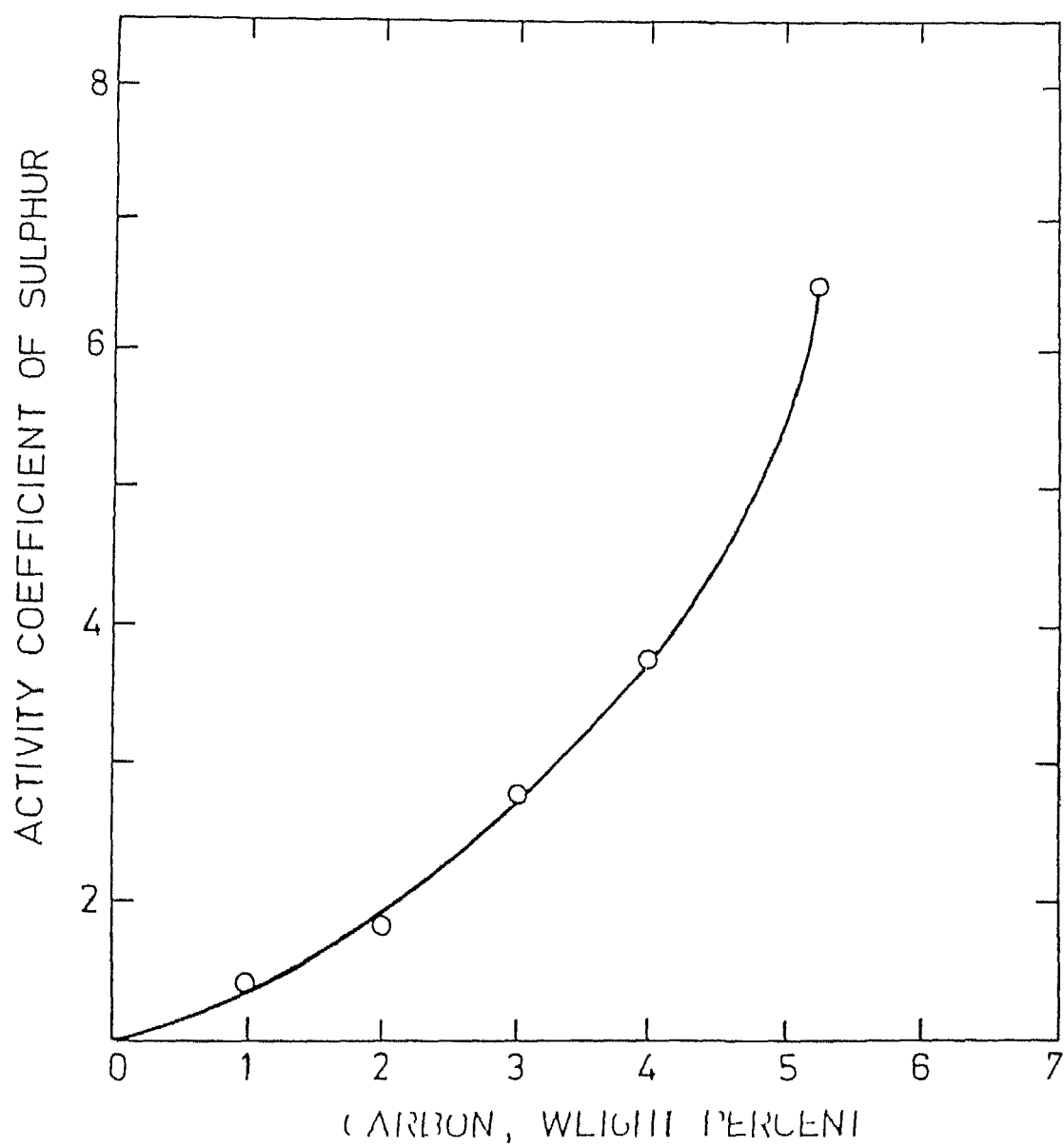
Figure 2 2   Effect of carbon content on activity coefficient of sulphur in iron at $1600^{0}C$

case using equation (2 7)   Their results are summarised in Table (2 1) and figure (2 3)

Table 2 1   Summary of interaction parameters obtained by Sherman and Chipman

i	$e_s^i = \frac{\partial \log f_s}{\partial wt\%i}$
C	+0 113
Si	0 065
P	0 043
Al	0 054
Cu	-0 013
Mn	0 025

2 1 5   Sulphide capacity of the slag

The principal equilibrium reaction between gas and slag may be represented by the following

$$1/2S_2(g) + (O^{2-}) = (S^{2-}) + 1/2O_2(g) \tag{2 19}$$
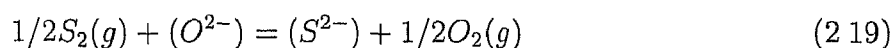
$$K = \sqrt{P_{O2}/P_{S2}} \ (a_S^{--}/a_O^{--}) \tag{2 20}$$

Richardson (4) assumed the henrian behavior of sulphur in slag because of its low solubility in slag and defined a term known as sulphide capacity as follows

$$C_s = sulphide\ capacity = (wt\%S)\sqrt{P_{O2}/P_{S2}} \tag{2 21}$$

Venkatradi and Bell (5) tried to express sulphur partition between slag and metal in the blast furnace melt in term of sulphide capacity of slag Sulphur distribution between slag and metal can be written as

$$(CaO) + [S] + [C] = CO(g) + (CaS) \tag{2 22}$$
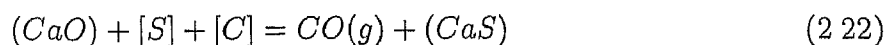
$$\log k = -5960/T + 6\ 022 \tag{2 23}$$
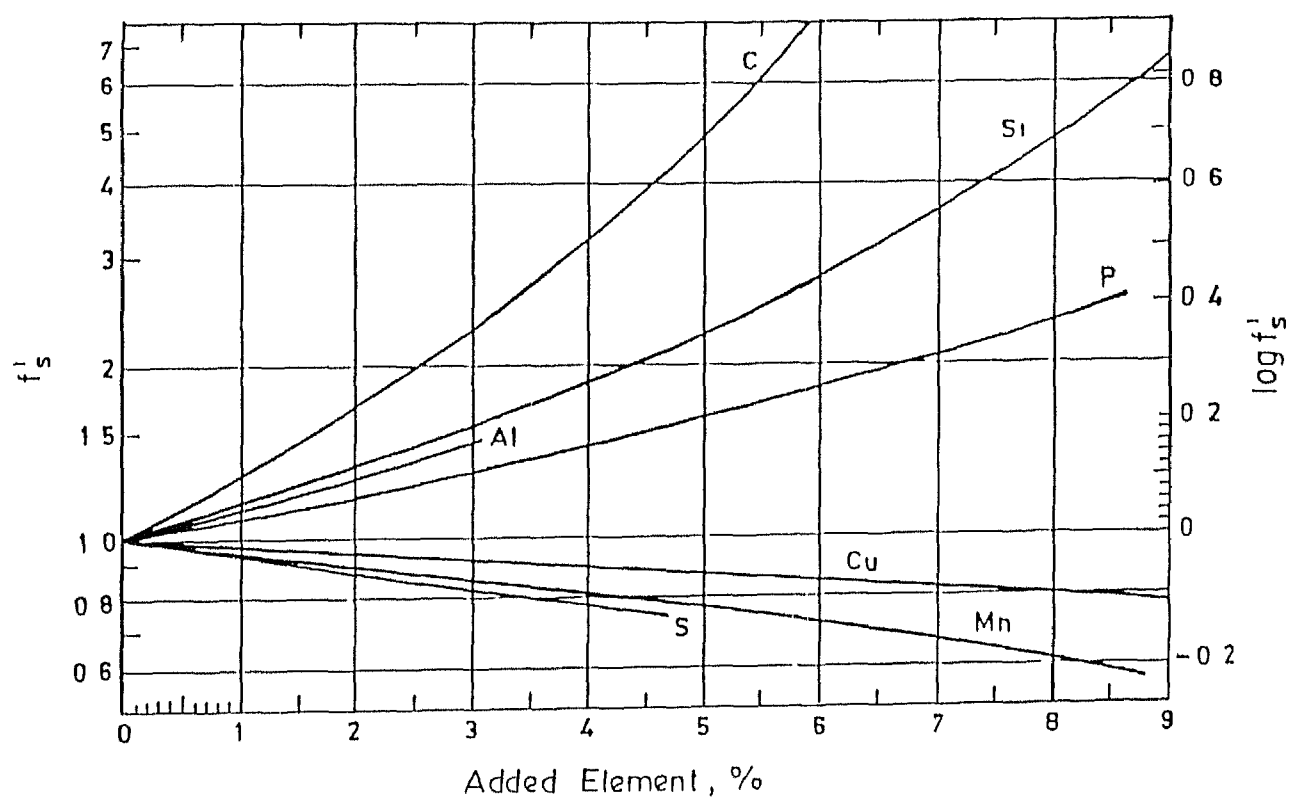
Figure 2 3   Effect of alloying elements on activity coefficient of sulphur in iron at $1600^{\circ}C$

They used the data of Kalyaniam (6) for sulphide capacities in different systems and correlated these data with empirically with ratio $\frac{(N_{CaO}+1/2N_{MgO})}{(N_{SiO_2}+1/3N_{Al_2O_3})}$ where N denotes mole fraction The plot between $\log C_S$ and $\frac{(N_{CaO}+1/2N_{MgO})}{(N_{SiO_2}+1/3N_{Al_2O_3})}$ at 1500°C is shown in Fig 2 4

Using the thermodynamic data for sulphur solution and carbon monoxide formation, they proposed a relation between sulphide capacity and sulphur partition ratio as follows

$$\log(\%S)/[a_S] = (5\ 55 - 7\ 24/T) + \log C_S + \log(a_C/P_{CO}) \qquad (2\ 24)$$

a_c and a_s are the activity of the carbon and the sulphur respectively Iron oxide content of slag is a better measure of oxygen potential than the carbon monoxide pressure Modifying the above equation, they obtained the following

$$\log(\%S)/[a_S] = (5543/T - 1\ 43) + \log C_S + \log(a_{Fe}/a_{FeO}) \qquad (2\ 25)$$

Kim Kaisud (7) studied the effect of alkali oxide on the sulphide capacity of the slag The oxides of potassium and sodium in the slag are of interest as alkali are well known to cause problems in the blast furnace iron making in blast furnace (8,9) They gave a relation where effect of MgO and alkali are put together

$$\log C_S = \log C_S^o - 0\ 01 * [Wt\%MgO - (wt\%MgO^o)] + 0\ 1 * [wt\%A - (Wt\%A^o)] \qquad (2\ 26)$$

where $wt\%A = 3$ wt% K_2O + wt% Na_2O

Subscript o stand for a reference value C_S^o refers to sulphur capacity in a reference state and $\log C_S^o$ was reported as $-3\ 82$ under the following conditions

Temperature 1500°C, basicity $B = 1\ 2$, 10wt% MgO, 12wt% Al_2O_3

$$\dfrac{N_{CaO} + 1/2 N_{MgO}}{N_{SiO_2} + 1/3 N_{Al_2O_3}}$$
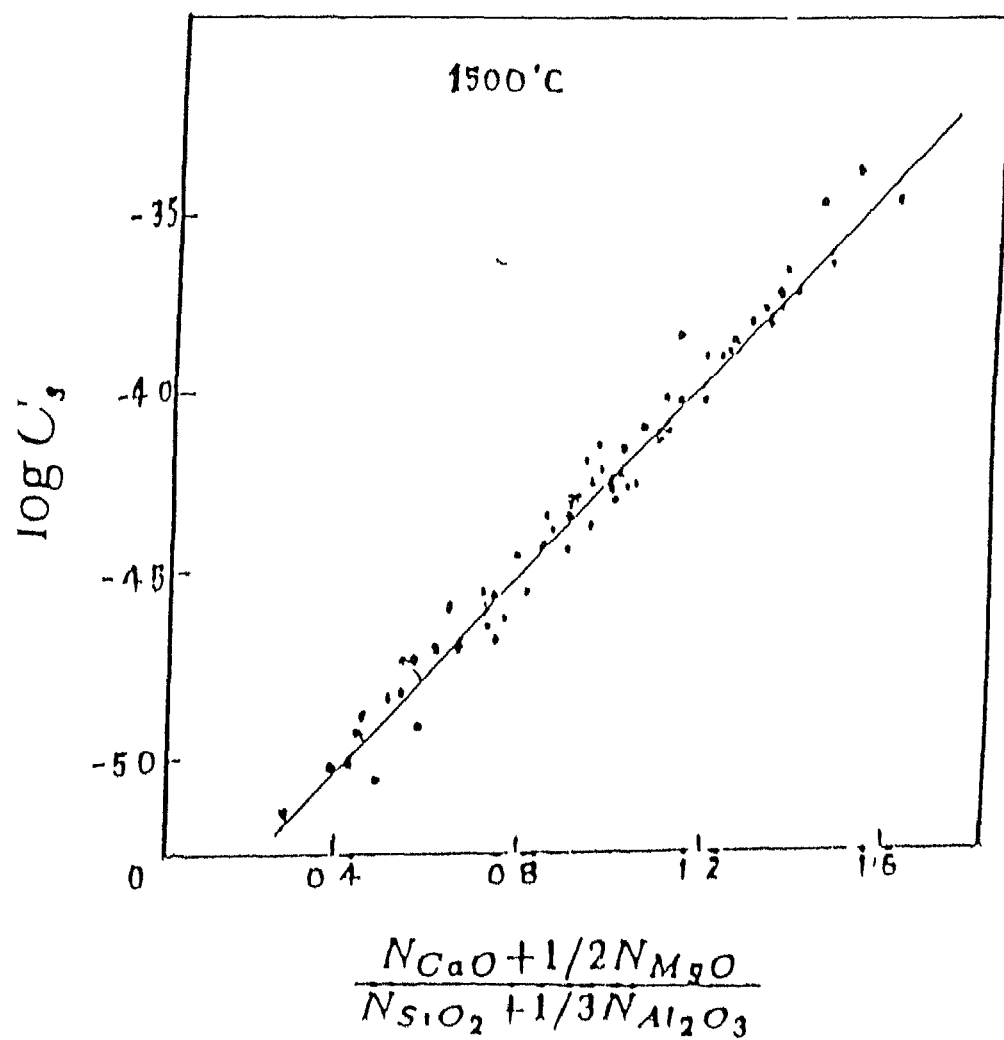
Figure 2 4 Correlation of sulphide capacity measurements with the empirical ratio

2 2   Sulpur distribution between metal and slag in blast furnace

Turkdogan (23) reviewed the reactions occurring in the blast furnace

The equilibrium reaction for distribution of silicon between metal and slag is given as

$$SiO_2(s) + 2C(gr) = [Si](1wt\%) + 2CO(g) \tag{2 27}$$

$$K_{Si} = \frac{[pctSi]\gamma'_{Si}p^2_{Co}}{a_{SiO_2}a^2_c} \tag{2 28}$$
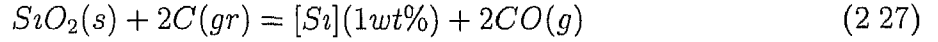
where γ'_{Si} is the activity coefficient of silicon whose value approaches to 15 for carbon saturated melt

In most of the blast furnace slags, the total number of moles of constituent oxides per 100 g of slag is about 1 65   Therefore, the activity of silica, SiO_2, can be represented in term of weight percent of SiO_2 and its activity coefficient, γ_{SiO_2}

$$a_{SiO_2} = \frac{(\%SiO_2)\gamma_{SiO_2}}{60 * 1\,65} \tag{2 29}$$

Combining (2 28) and (2 29) and assuming $a_C = 1$ and $[Si] < 2pct$

$$\frac{[\%Si]p^2_{SiO_2}}{(\%SiO_2)} = 7\,73 * 10^{-4}K_{Si}\gamma_{SiO_2} \tag{2 30}$$

the value of γ_{SiO_2} for $CaO - Al_2O_3 - SiO_2$ melt at 1500^0C may be obtained from work of Rein and Chipman (24)   The temperature dependence of K_{Si} is given as

$$\log K_{Si} = \frac{-30935}{T} + 20\,455 \tag{2 31}$$

The equilibrium constant for reduction of MnO is evaluated as

$$MnO + C(gr) = [Mn] \qquad + CO(g) \tag{2 32}$$
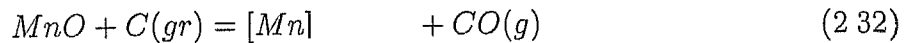
$$K_{Mn} = \frac{[\%Mn]\gamma'_{Mn}p_{CO}}{a_{Mn}a_C} \tag{2 33}$$

An estimated value of $\gamma'_{Mn} = 0\,8$ may be used for graphite saturated melt In term of γ_{MnO}, and weight percent MnO

$$a_{MnO} = \frac{(\%MnO\gamma_{MnO}}{71 * 1\,65} \tag{2 34}$$

Abrahm et al (25) have calculated the activity coefficient of MnO γ_{Mno} in $CaO - Al_2O_3 - SiO_2 - MnO$ slag at $1500^\circ C$ and $1600^\circ C$

For unit activity of carbon we have

$$\frac{[\%Mn]p_{CO}}{(\%MnO)} = 1\,07 * 10^{-7} K_{Mn}\gamma_{MnO} \tag{2 35}$$

Temperature dependence of equilibrium constant K_{Mn} is given as

$$\log K_{Mn} = \frac{-15090}{T} + 10\,970 \tag{2 36}$$

In the blast furnace, the sulphur reaction may be represented by

$$CaO(s) + [S](1wt\%) + C(gr) = CaS(s) + CO(g) \tag{2 37}$$
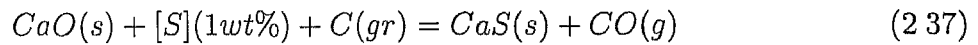
$$K_S = \frac{a_{CaS}p_{CO}}{a_{CaO}[\%S]\gamma'_S a_C} \tag{2 38}$$

The temperature dependence of the equilibrium constant, K_S, is given by

$$\log K_S = \frac{-6010}{T} + 5\,935 \tag{2 39}$$

The activity of CaS and CaO relative to pure solids may be represented in term of weight percent of CaS and CaO and their activity as

$$\frac{a_{CaS}}{a_{CaO}} = \frac{56(\%S)\gamma_{CaS}}{32(\%CaO)\gamma_{CaO}} \tag{2 40}$$

In a graphite saturated melt,   the activity coefficient of sulphur , γ'_S around $7_{\color{white}s}$ Inserting this in equation (2 38) and combining this with (2 40)we have

$$\frac{(\%S)p_{CO}}{[\%S]} = 4\frac{\gamma_{CaO}(\%CaO)K_S}{\gamma_{CaS}} \tag{2 41}$$

Ratio of $\frac{\gamma_{CaO}}{\gamma_{CaS}}$ derived from data of Abrahm(26)
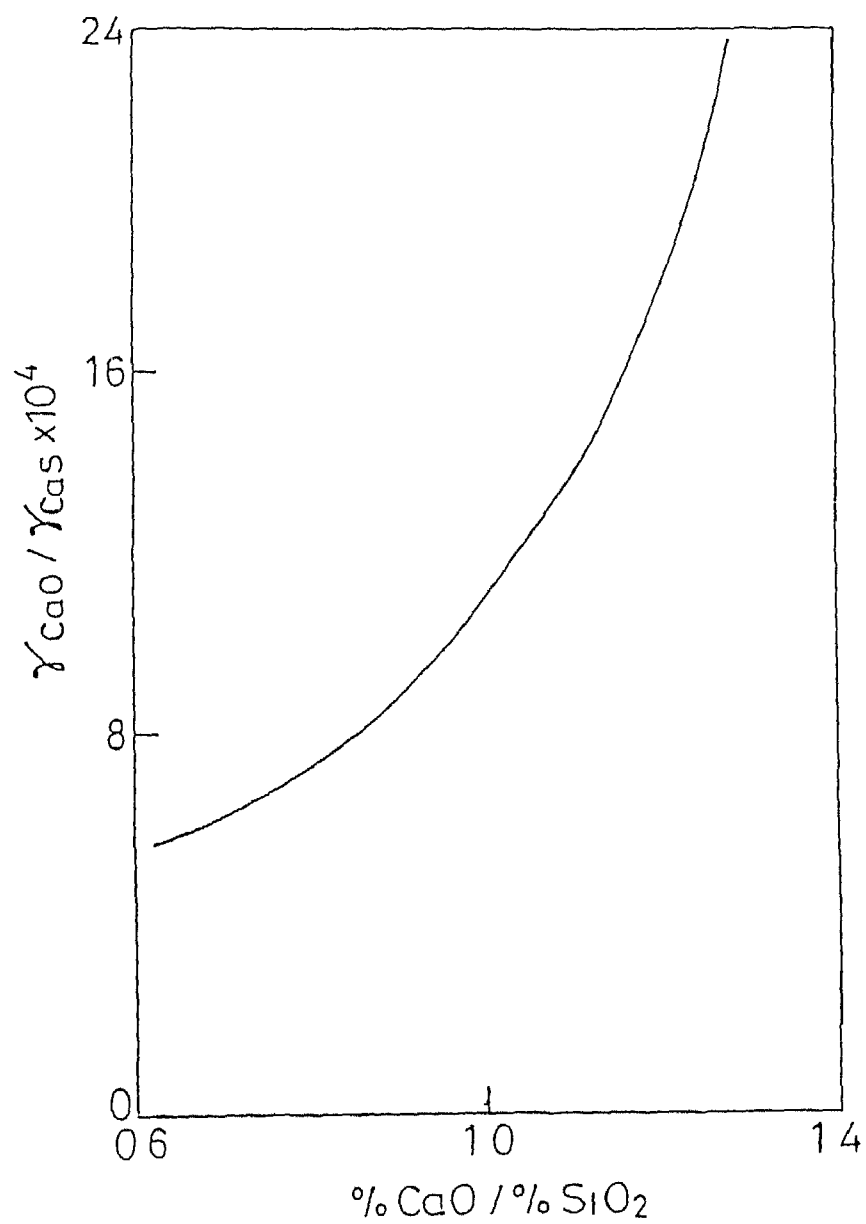
Figure 2 5   Lime / Sulphide activity coefficient ratio at $1500^{0}C$ in calcium silicate melt saturated with CaS

Turkdogan (26) as well as Biswas (27) has shown that the primary reactions for the transfer of manganese, silicon and sulphur from metal to slag do not reach equilibrium in blast furnace due to three phases involved in these reactions. However, coupled reactions more or less reach equilibrium in the blast furnace. Some important coupled reactions are described in the following section.

1 Reaction involving manganese and sulphur is:

$$CaO(s) + [Mn] + [S] = CaS(s) + Mno(s) \qquad (2.42)$$
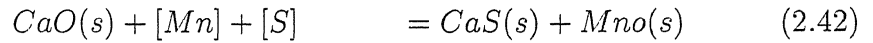
$$K_{MS} = \frac{K_S}{K_{Mn}} = \frac{a_{CaS} a_{MnO}}{a_{CaO}[\%S][\%Mn]\gamma'_{Mn}\gamma'_S} \qquad (2.43)$$

Combining this with equation (2.33), (2.39) and (2.40) gives

$$\frac{(\%S)}{[\%S} = 374(\frac{K_S \gamma_{CaO}\%CaO}{K_{Mn}\gamma_{CaS}\gamma MnO})\frac{[\%Mn]}{(\%MnO)} \qquad (2.44)$$

2 Reaction involving silicon is given as

$$CaO(s) + \frac{[Si]}{2} + [S] = CaS(s) + \frac{SiO_2}{2} \qquad (2.45)$$
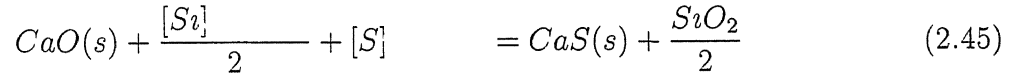
$$\frac{(\%S)}{[\%S]} = 154\frac{K_S\gamma_{CaO}\%CaO}{\sqrt{K_{Si}}\gamma_{CaS}\sqrt{\gamma_{SiO_2}}}\frac{\sqrt{[\%Si]}}{\sqrt{(\%SiO_2)}} \qquad (2.46)$$

The graph between $\frac{(\%S)}{[\%S]}$ vs. $\frac{[\%Mn](CaO)}{(\%MnO)}$ is given in Fig (2.6). With the given data, sulphur-manganese equilibrium at graphite saturation is represented as

$$\log \frac{(\%S)(\%MnO)}{[\%S][\%Mn]} = 9080/T - 5.832 + \log(\%CaO) \qquad (2.47)$$

For sulphur-silicon reaction, the equilibrium relation may be given as

$$\log \frac{(\%S)\sqrt{\%SiO_2}}{[\%S]\sqrt{[\%Si]}} = 9080/T - 5.832 + \log (\%CaO) + 1.396B \qquad (2.48)$$
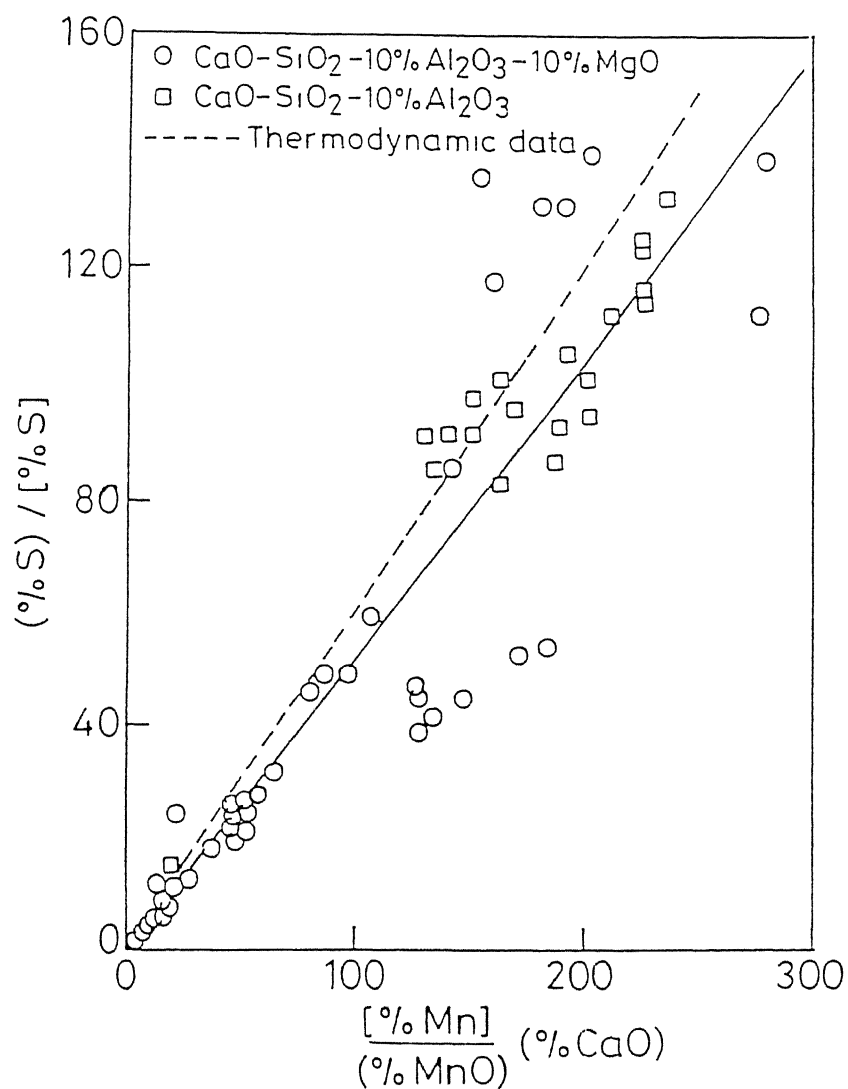
Figure 2 6· Sulphur — manganese reaction equilibrium at graphite saturation and $1500^0 C$

2.3   Mechanism and Kinetics of Desulphurization

King and Ramachandran (10) have demonstrated that the transfer of sulphur to carbon saturated-non-slag system is electrochemical in nature. When the sulphur is transferred from metal to slag, electrons must be provided as given below.

$$S + 2e^- = S^{2-} \tag{2.49}$$

Since the electroneutrality is maintained in the slag and the metal in the absence of an electric field across the slag metal interface, the solute in the metal becomes oxidised to provide election needed for the necessary requirement as follows.

$$Fe = Fe^{2+} + 2e^- \tag{2.50}$$

$$O = O^{2-} - 2e^- \tag{2.51}$$

$$Si = Si^{4+} + 4e^- \tag{2.52}$$

$$Mn = Mn^{2+} + 2e^- \tag{2.53}$$

$$C + O^{-2} = Co + 2e^- \tag{2.54}$$

$$Al = Al^{3+} + 3e^- \tag{2.55}$$
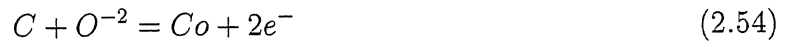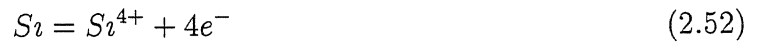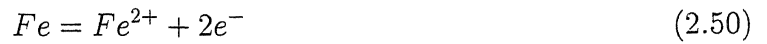
Therefore, in presence of these solutes in iron, the transfer of n_S moles of sulphur from metal to slag is always accompanied by the transfer of an equivalent moles of solutes to satisfy the stoichiometric requirement. The balance is given as

$$2n_S = 2n_{Fe} + 2n_{Mn} + 3n_{Al} + 4n_{Si} + 2n_c \tag{2.56}$$

J C. Fulton (11) have studied the effect of stirring on the desulphurization rate. To analyse their data, they assumed that transfer of sulphur from bulk metal to phase boundary controlled the rate of overall reaction and they obtained following expression

for transfer of sulphur from metal to slag phase .

$$\frac{V dC'_S}{dt} = -\frac{D'_S A (C'_S - C^*_S)}{\delta'_S}$$
(2 57)

$$2.3 \frac{d \log(C'_S - C^*_S)}{dt} = -\frac{D'_S * A}{\delta'_S V}$$
(2.58)

where C'_S = concentration of sulphur in the bulk metal at any time in $moles/cm^3$

C^*_S = equilibrium concentration of sulphur in the metal.

D'_S = diffusion coefficient of sulphur in the metal.

δ'_S = effective boundary layer thickness for sulphur in the metal.

A = area of the slag metal interface.

V = volume of metal.

t = time

For simple geometry V/A = L and expressing concentration in $Wt\%$, δ'_S can be calculated from the slope of $\log([\%S] - [\%S^*])$ vs time as follows.

$$\delta'_S = \frac{D'_S}{2.3 * L * slope}$$
(2.59)

Then, results are plotted in Fig (2.7) from which it is clear that stirring rate effects the kinetics of reaction They found that in the early stages of each experiment curve is non - linear This is attributed to increase in slag -metal interfacial area.

In a review paper on equilibrium and kinetics of slag metal reaction, Yasuji (12) examined effects of various factors on the rate of desulphurization. Fig. (2.9) shows the effect of slag composition on the rate of desulphurization. The rate can be expressed as the first order reaction It was found that the rate increased with an increase in the basicity of slag. Mathematically one may obtain the following.

$$\frac{W_S}{100A} \frac{d\%S}{dt} = K_m[\%S] - K_S[\%S]$$
(2.60)

K_m and K_S are the mass transfer coefficent for sulphur in the metal and slag phase respec-
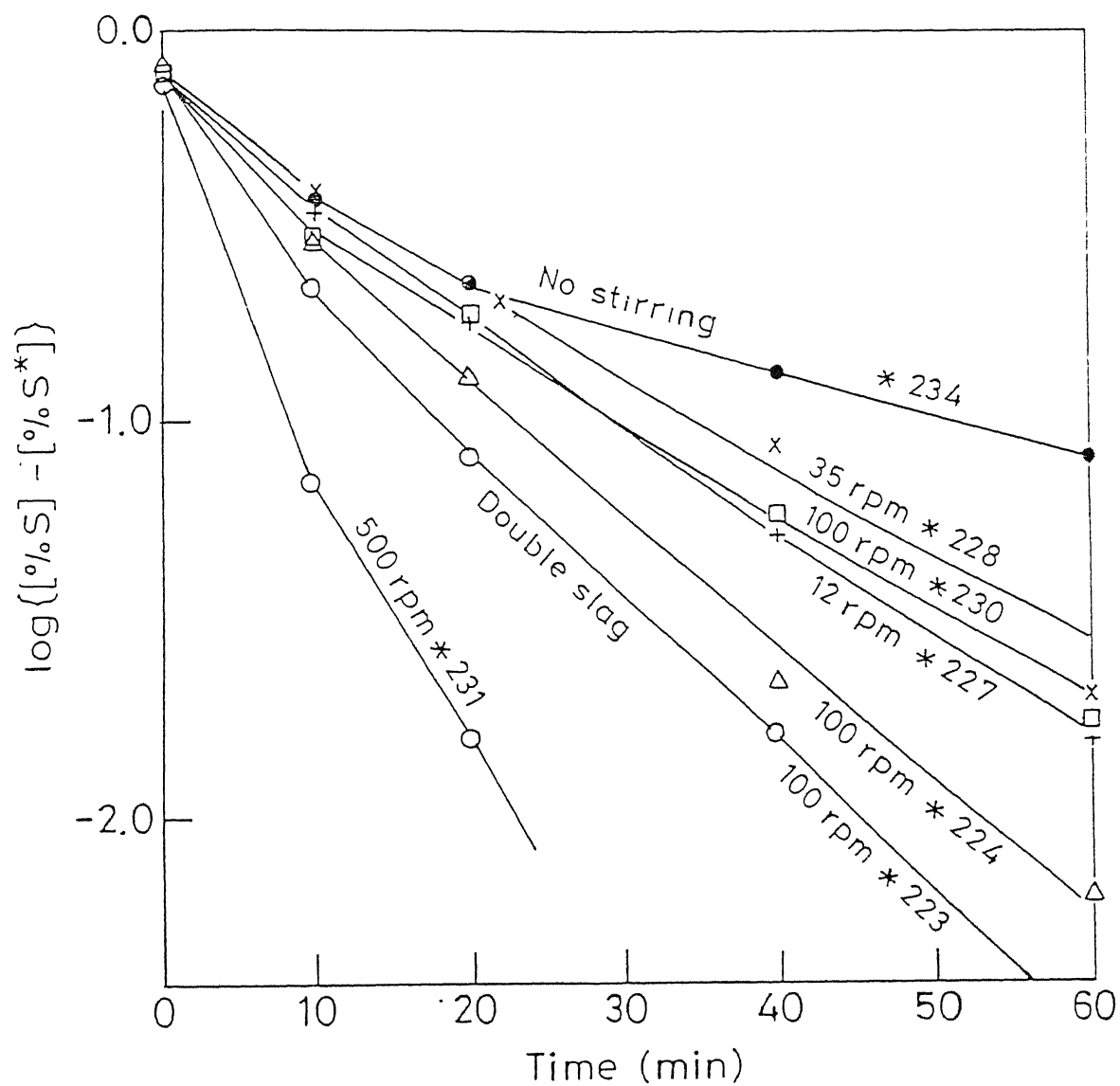
Figure 2 7· Effect of stirring on the desulphurization rate

tively Values of K_m and K_s as obtained by them are plotted against slag basicity in Fig. 2.8

K_m increases with increasing slag basicity, but K_S decreases The fact that rate depends

on slag composition suggests that desulphurization process depends upon the diffusion of

sulphur in the slag Desulphurization rate can be expressed as follows.

$$\frac{d\%S}{dt} = -\frac{A * D_S * \rho_s}{V_m * \delta_s * \rho_m} * ([\%S]^i - [\%S])$$ (2.61)

Where ρ_s and ρ_m are densities of iron and slag, D_S is the diffusivity of sulphur in the slag,

δ_s is the thickness of boundary layer of slag·

Frohberg (13) studied the kinetics of sulphur transfer from metal containing different amount

of C, S, Mn, Al, Si and Ti to lime silica slag at 1600°C. They found that the presence of Al,

Ti, Mn and Si in metal increases the rate of desulphurization. They also found reversion of

Fe, Mn, Ti from slag to metal phase . To explain their observations, a mechanism of sulphur

transport was proposed .It consists of the following three steps.:

1)Transfer of sulphur and other reactants from the bulk to slag metal interface.

2)Reaction at the interface.

3)Transport of products away from interface.

It was assumed that interfacial reaction controlled the rate of transfer of sulphur as the

activation energy for interfacial reactions was much higher than that for transport phenomena

They proposed that desulphurization process could be expressed through the following rate

equation.

$$J_s^i = 1/2 \sum_{i=1}^{N} Z_i [K_i a_i^M \exp(\frac{Z_i(\mu_S^{M'} - \mu_S^{s'})}{Z_S RT}) - K_i a_i^S \exp(-\frac{Z_i(\mu_S^{M'} - \mu_S^{S'})}{Z_S RT})]$$ (2.62)

where a_i^M and a_i^S =activity of element i in metal and slag phase respectively.

J_i^t = Transport rate of component i

K_i = specific reaction rate of element i

Z_i = charge on element i

R = gas constant

T = absolute temperature
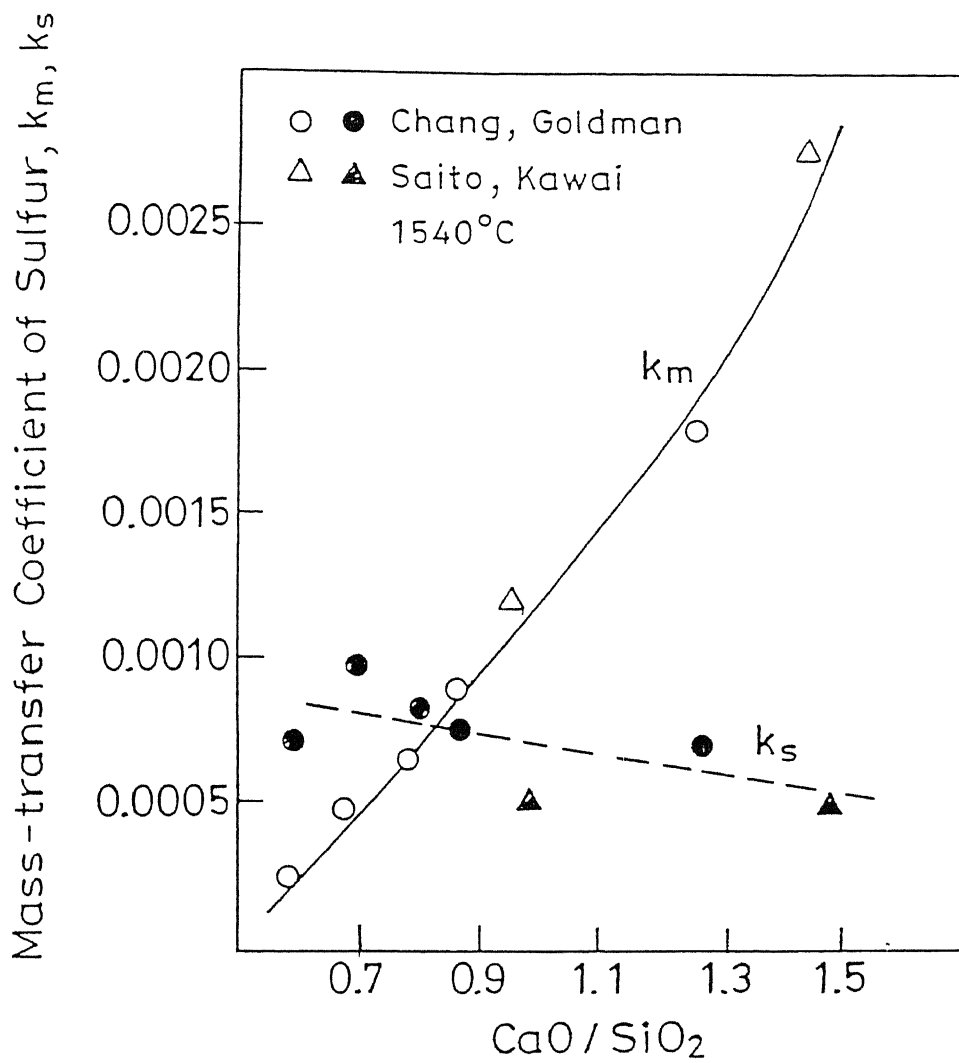
Figure 2.8. Relation between mass transfer coefficient , K_m and K_s , and basicity of slag
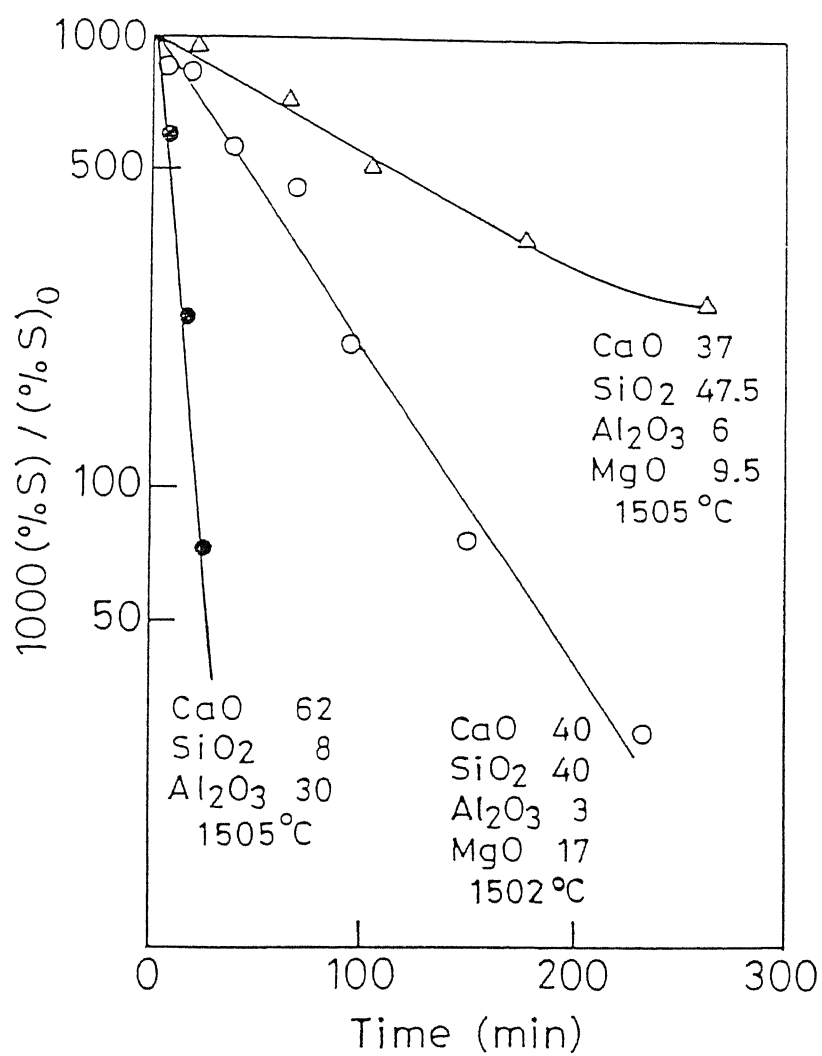
Figure 2 9· Concentration change of sulphur in liquid iron in slag of different basicities

$\mu_S^{M'}$ and $\mu_S^{S'}$ = Chemical potential of the sulphur at the interface in metal and slag phases respectively

2.4   External Desulphurization of Hot metal

Due to importance of external desulphurization of hot metal,many studies on the kinetics of desulphurization by injection of calcium carbide, magnesium, lime and calcium alloys etc in the blast furnace iron have been reported in the literature These studies are helpful in enhancing our knowledge of desulphurization process from industrial point of view. Most of these studies are done on pilot plant scale.The various methods of pretreatment of metal are summarised in Table 2.2.

Table 2.2: Method of desulphurization

Desulphurizing agent	Mode of addition	Reagent quantity kg / THM	Sulphur range
Soda ash	bulk addition	10	0.10 to 0.035
Lime	injection	10 to 20	0.05 to 0.02
lime and soda ash	injection	8 to 10	0.05 to 0.02
Calcium carbide	injection	4	0.05 to 0.02
Magnesium coke	plunging	0.7	0.048 to 0.022
Magnesium granules	plunging	0.7 to 1.2	0.05 to 0 005

Lime is capable of reducing sulphur content of cast iron and blast furnace iron to very low level but the rate of desulphurization is low.It may be attributed to solid reaction products that form a diffusion barrier on the surface of lime particles .

Craig F Landefeld (14) have studied effect of lime and spar addition in the melt. Results are plotted in Fig (2.10).Addition of spar increases the rate of desulphurization. However, under the experimental conditions, the rate of desulphurization was found to remain un-

changed beyond 8% spar This is attributed to saturation of liquid phase with $3CaO.SiO_2$ phase They also compared the effects of Si and Mn on desulphurization rate. Results are plotted in Fig (2 11). Magnesium is used to desulphurize the metal from blast furnace iron However, injection of magnesium into blast furnace iron has been a major problem Boiling point of magnesium is 1107^0C and it tends to explode when plunged into hot metal whose temperature commonly exceed 1200^0C. Iron et al. (15) have circumvented the problem by vapourizing the magnesium before it was injected into iron and studied the kinetics of desulphurization, based on MgS precipitation.

External desulphurization of hot metal by calcium carbide injection in the melt is a well established process Chang (16) have studied the kinetics of desulphurization of hot metal at temperature of 1350^0C and reported that the oxygen activity of the bath is very important factor during desulphurization Control of hot metal oxygen activity to low levels improved the efficiency of desulphurization process. They found that there was an incubation period during which reagent created an appropriate slag layer before it began to remove the sulphur.

With no slag, the melt surface was susceptible to oxidation and a liquid layer of iron oxide was probably formed This slag could then oxidize the calcium sulphide produced during the desulphurization process thus reverting the sulphur into iron melt. The net effect was that no desulphurization occurred in the incubation period. As the partially oxidized CaC_2 / CaS particles continued to build up on the surface during injection, conditions would become more and more reducing, thereby favouring desulphurization. In case of unreactive slag mixture of $CaO - SiO_2$, an oxide rich slag could be formed, which must be reduced before effective desulphurization could proceed.

Tabala (17) proposed a reaction mechanism according to which calcium carbide first decomposed to from graphite and calcium vapors. The calcium vapors then reacted with sulphur to form a layer of calcium sulphide over the graphite layer. The layers of graphite and calcium sulphide progressively thicken so that calcium vapour must diffuse through them . Chiang et al. (18) showed that the rate of calcium diffusion through the product layer was 50
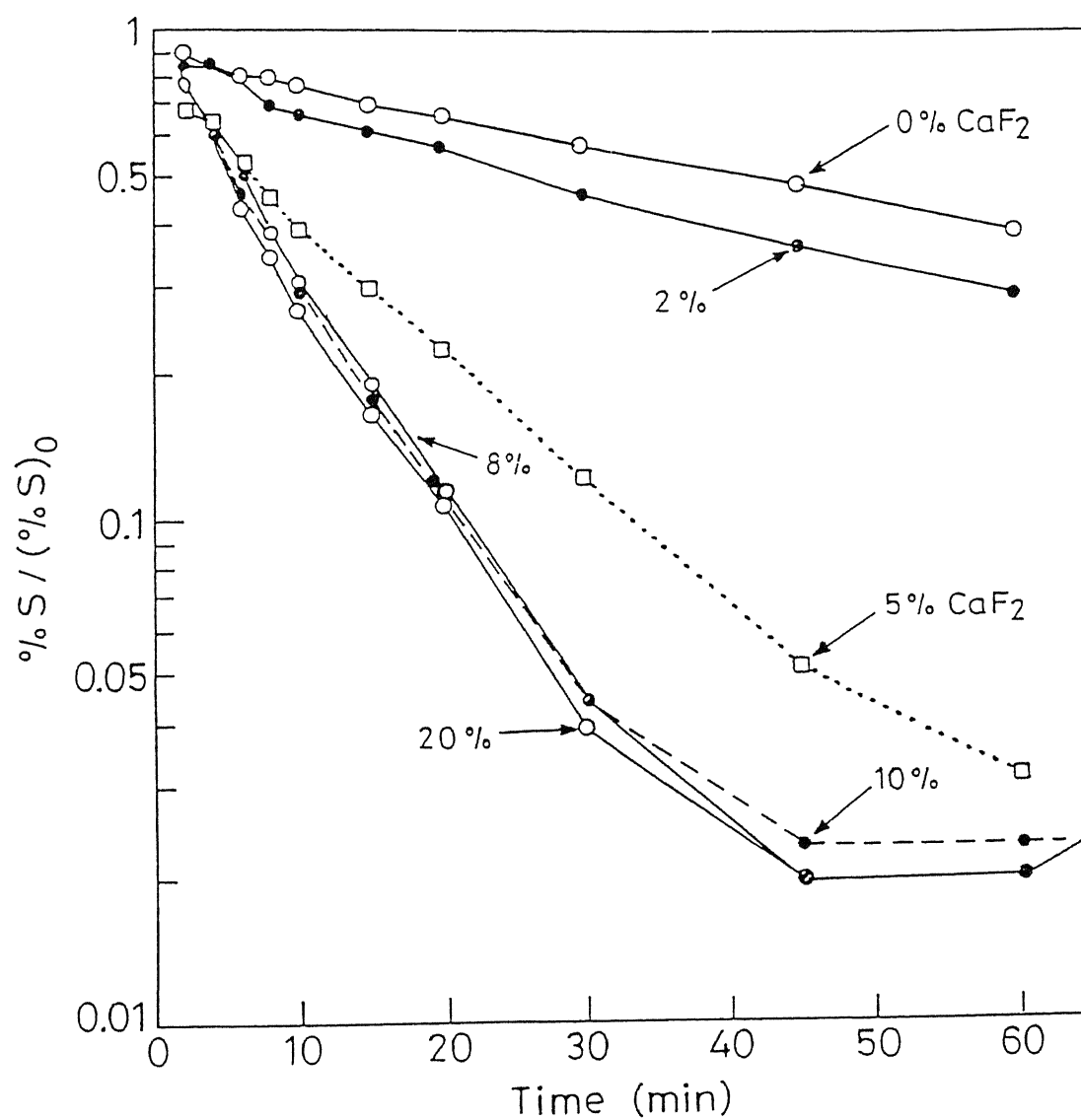
Figure 2 10 Effect of CaF_2 percentage on desulphurization
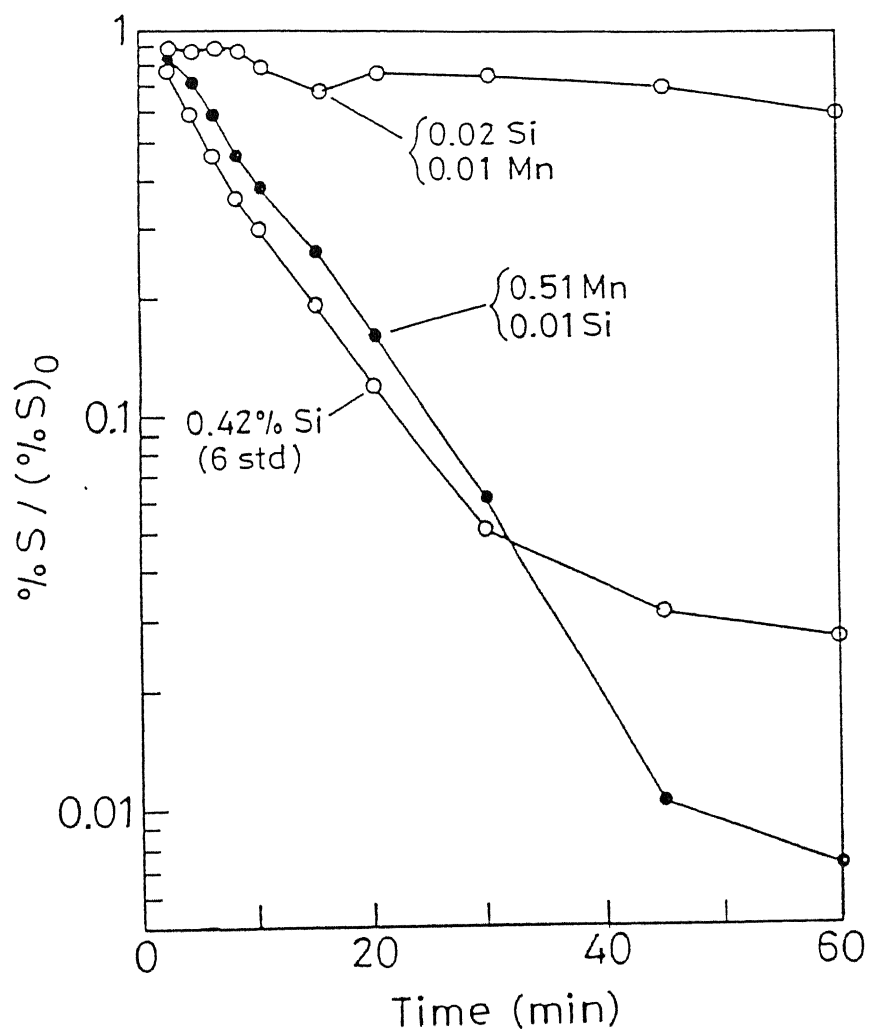
Figure 2.11· Comparison of the effects of Si and Mn

times greater than the rate of sulphur diffusion through the particle/liquid boundary layer. Based on these facts, they concluded that desulphurization rate was determined by   the rate at which sulphur diffused through the liquid boundary layer around the particles rather than the product layer.

External desulphurization process has some limitation which may be due to inherent difficulties encountered during external desulphurization process. Some of the problems that are encountered are below:

(1) Freezing of top layer of metal in the ladle may occur to give high skull losses This makes addition of desulphurizing agent to bath very difficult.

2) Sulphur rich blast furnace slag may accompany the metal. In some cases it may lead to increase in the sulphur in sulphur load

3) Ladle lining may get damaged due to addition of desulphurizing agents .

4) limitation on effectiveness of desulphurizing agents makes the process plant specific.

2.5   Effect of Manganese on desulphurization

Oelsen (19) studied the solubility of MnS in carbon saturated blast furnace iron and reported that the solubility of MnS decreased with decreasing temperature . Results are plotted in Fig (2 11). Si and P content of the blast furnace iron was not specified by Oeslen. Morris (20) studied Mn-S equilibrium in Fe-C alloys by step wise addition of manganese. His results are plotted in Fig (2.12).

Morris concluded from his data that manganese alone could not be an efficient desulphurizer except at temperature below the normal operating range. However, he predicted that in presence of an oxide slag, manganese could be a more effective desulphurizer due to lower activity of manganese sulphide in the slag. Grant (21) studied the the effect of Mn and MnO when added to initial charge or during the course of a heat. Addition of MnO led to an immediate and temporary reversion of sulphur to the melt. This was ascribed to the increase in oxygen potential of slag. Effect of Manganese on desulphurization rate was very small and it
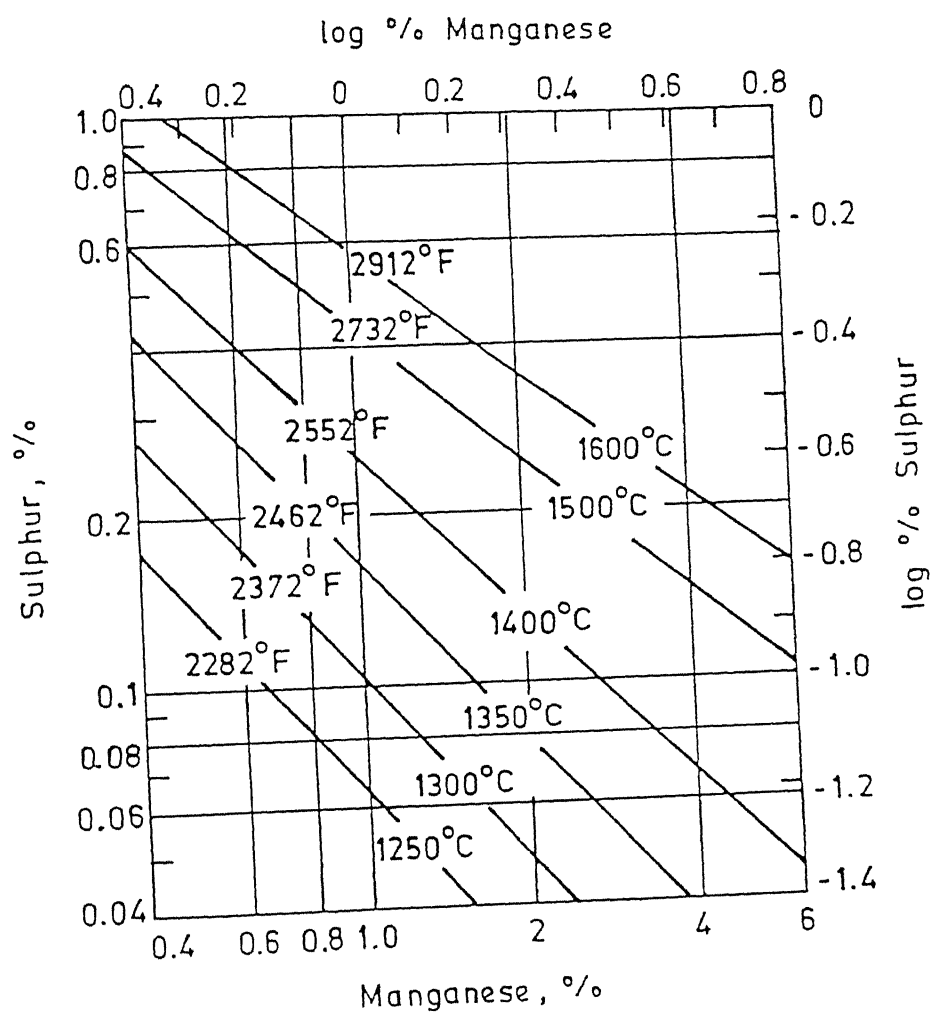
Figure 2.12· manganese sulphide solubility in the Iron-carbon melt
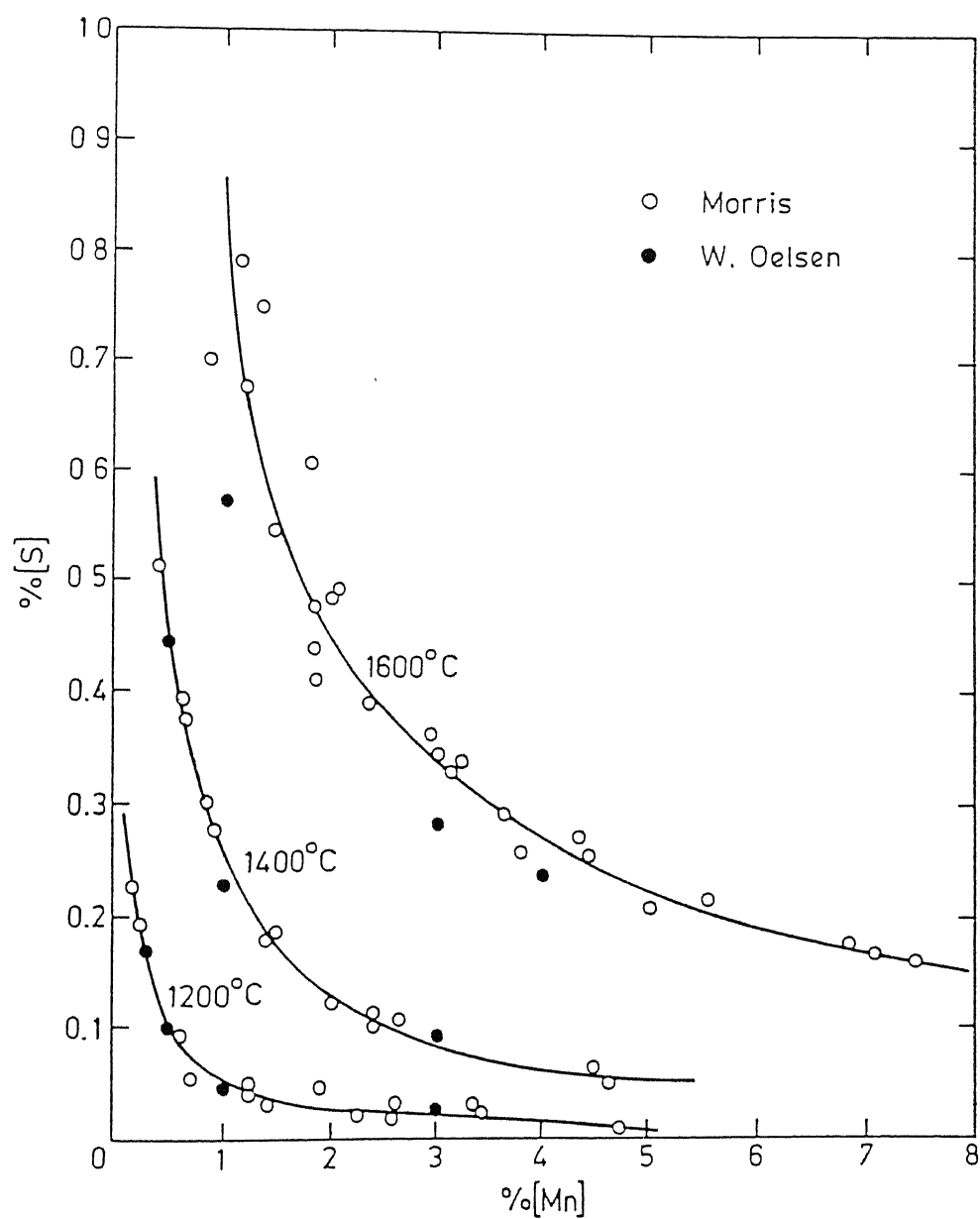
Figure 2.13: Effect of manganese on the sulphur content of the carbon saturated melts of iron in equilibrium

was confined to less basics slags. Pattjoshi (22) showed that with an increase in manganese level in the melt, there was increase in transfer of sulphur to slag phase. Following reasons were attributed to this;

1 The activity of MnS was lowered due to presence of liquid lime based slag.

2 Manganese enhanced the rate of sulphur removal by CaO in the slag as per the following reactions

$(CaO) + S = (CaS) + [O]$

$[O] + Mn = (MnO)$
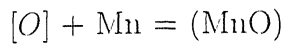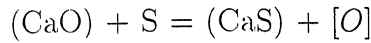
(3)Manganese in the melt reacted with SiO_2 in the slag to form silicon in the melt and MnO as per the reaction

$2[Mn] + SiO_2 = 2 Mno + [Si]$
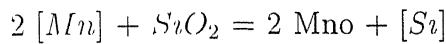
This would increase the basicity of the slag which lowers sulphur in the melt.

He suggested that all the three factors listed above might be responsible for lowering of sulphur level in presence of manganese in the melt.

Chapter 3

EXPERIMENTAL DETAIL

3.1 Materials

Solid pig iron samples were obtained from Bhilai Steel Plant They were broken into small pieces so that they could be charged to the graphite crucible Manganese used was 99% pure in the form of flakes. Iron sulphide, silica and alumina used in the study were of GR grade Lime used was obtained from Ranbaxy India Limited 4 mm dia and 500 mm long quartz tubes were used to draw samples One tube could be used for drawing 3 to 4 samples Standard steel and cast iron sample supplied by NML, Jamshedpur were used to calibrate the set up to determine manganese and sulphur in samples, 50-60 mm high graphite crucible were machined from 50 mm dia, graphite rod

3.2 EQUIPMENTS

3.2.1 Super Kanthal Raising Hearth Type Furnace

One raising hearth type furnace i e , model 70 R 10 manufactured and installed by Bysakh and Company, Calcutta was used for doing a series of experiments in the present study. It has got dimensions of 200 mm square × 300 mm high. The furnace consists of 3 numbers of U shape Molybedum Disilicide heating elements of type `33' The furnace has got Pt - 6% Rd/Pt - 30% Rd thermocouple for temperature measurements and a proportional temperature controller. The furnace required a power supply of 2 phase AC of 400 volt. The furnace bottom has a opening of 120 mm and its refractory end was raised or lowered using a lever arm for closing and opening the furnace bottom respectively.

3.2.2 Silicon Carbide Furnace

One silicon carbide furnace having outer diameter of 600 mm and length 400 mm was fabricated in the laboratory Schematic of the furnace is shown in Fig 3 1. The furnace tube consisted of an alumina tube of 65 mm i.d and 600 mm long, with one end closed. It rested on a refractory base at the bottom The tube was filled with alumina powder upto the level of high temperature zone in the furnace The power to the furnace was supplied using a 40 A single phase oil cooled auto-transformer with 220 volts input and 0 - 240 volt output Pt - Pt - 10% Rh thermocouple was used to measure and control the temperature One on - off temperature controller and magnetic relay switch were used to keep the temperature of the furnace in a narrow range

3.2.3 Digital Balance

The digital balance supplied by the Mettler, Germany, was used to determine the weight upto the accuracy of 0 1 mg for doing chemical analysis of the samples for sulphur and manganese determination.

3.2.4 Sulphur Analysis Set-up

Schematic of the apparatus used to determine sulphur content of samples is shown in Fig. 3 2. It consists of 500 cc conical flask, B/34 sealing joints, separating funnel, 6 mm dia glass tubing, 100 cc measuring cylinder and 1500 watts hot plate. Titration set up consisted of a 25 cc burrete and a 10 cc pipette.
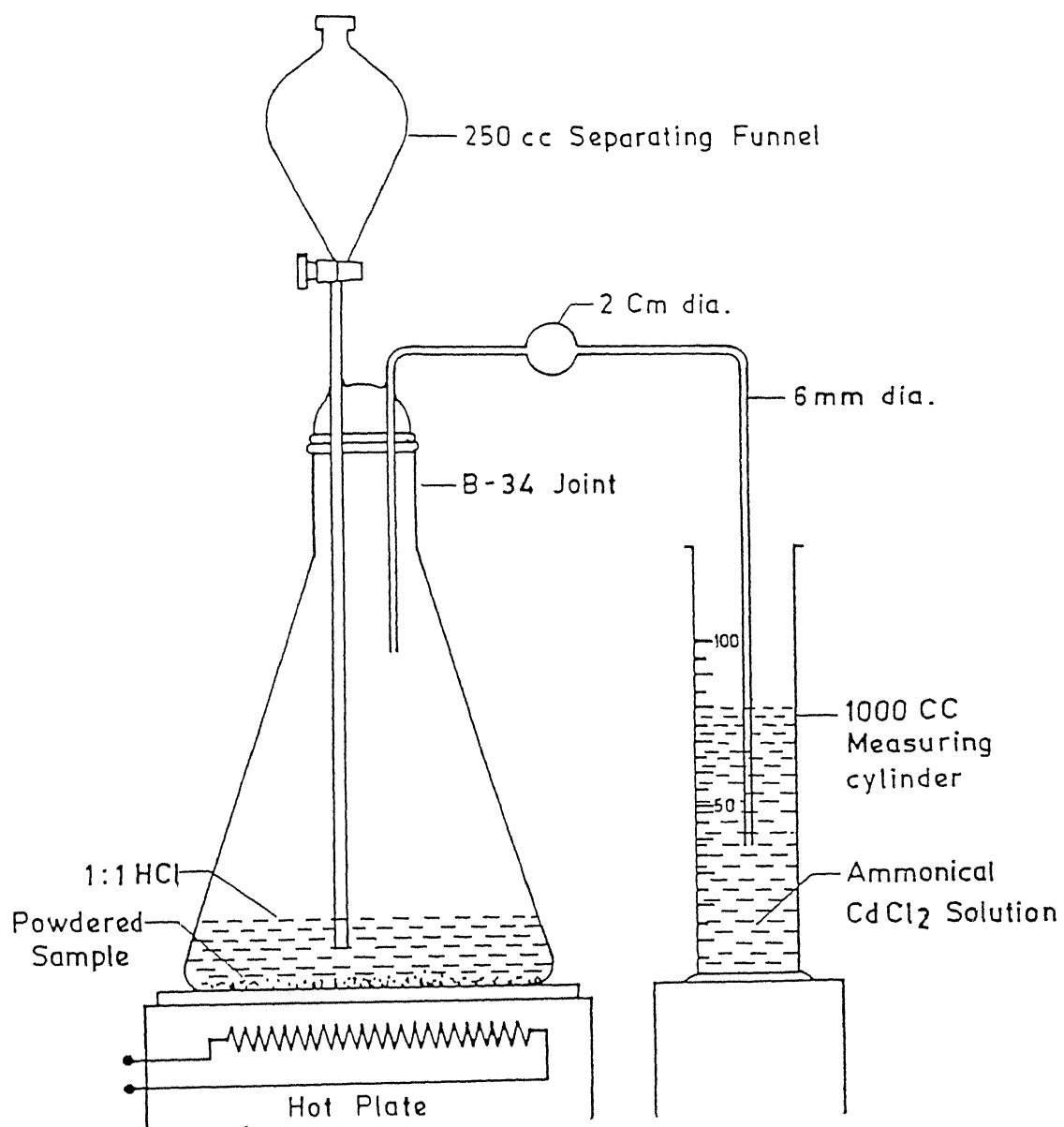
Figure 3 2: Schematic set up for sulphur analysis
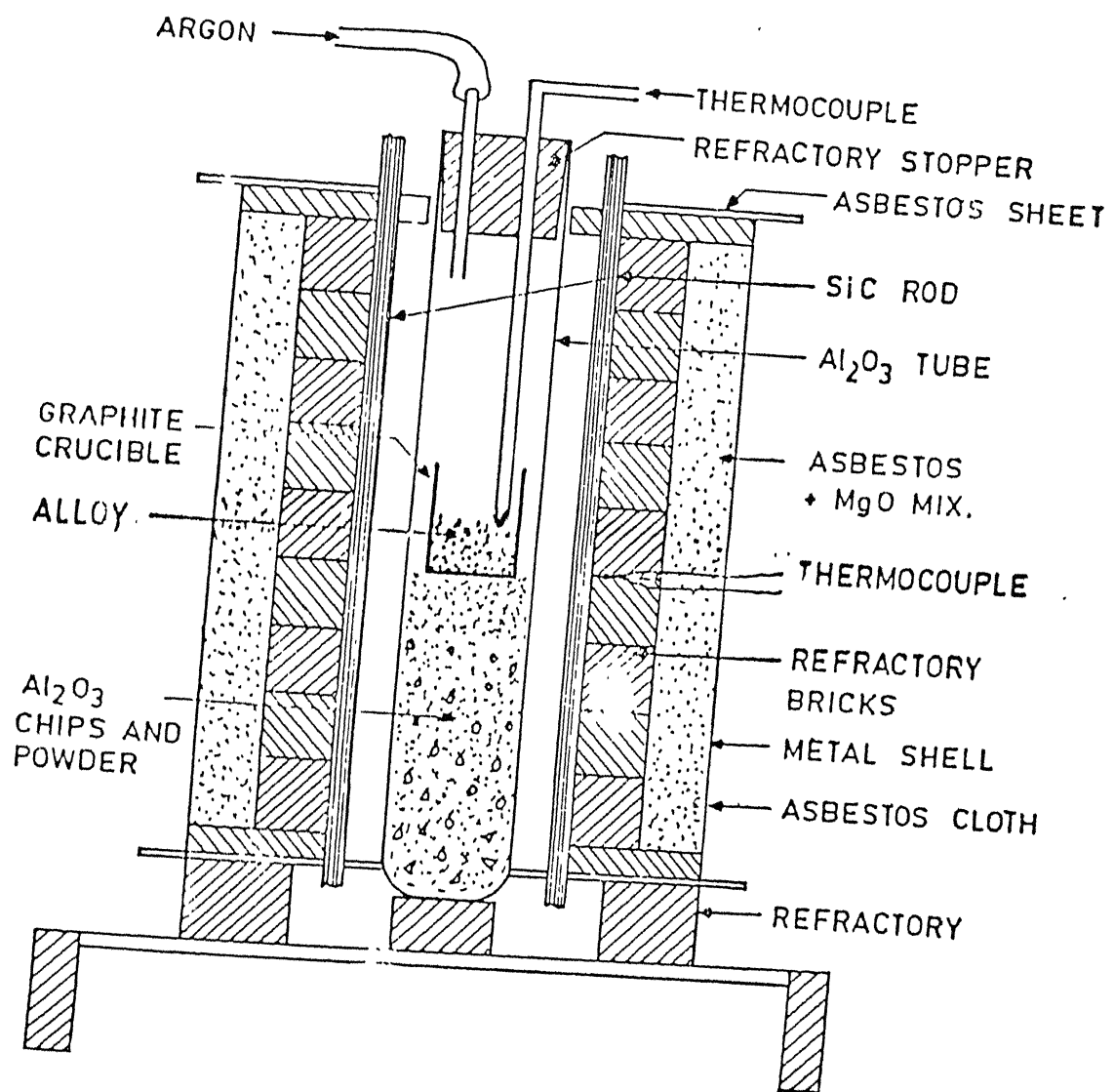
Figure 3.1: Schematic diagram of silicon carbide furnace

3.2.5 Photospectro meter

Manganese analysis was done using Ultra-Violet-Visible Range Spectro-photometer supplied by Systronics, New Delhi

3.2.6 Flow Meter

One capillary flow meter was used to determine flow rate of argon The flow meter was calibrated using a soap bubble meter

3.3   Experimental Procedure

3.3.1 Master Slag Preparation

One master slag was made in the laboratory by melting 10 g of alumina, 20 g of lime and 20 g of silica in a graphite crucible. The crucible was heated to 1500°C and held there for 2 h before cooling it to room temperature The slag was recovered by breaking open the crucible.

3.3.2 Melting of Metal and Slag Phase in Silicon Carbide Furnace

80 to 100 g of blast furnace metal pieces along with required additives such as iron sulphide, manganese metal and slag components were added to a graphite crucible The crucible was lowered into the hot zone of the silicon carbide furnace using a steel rod. The temperature of furnace was 800°C at the time of lowering the crucible. Argon gas was passed at the rate of 4 cc per second using a silica tube Argon flow was maintained throughout the duration of the experiment except for a few minutes when samples were drawn in a quartz tube using an aspirator The furnace was maintained at the required

temperature for the specified duration of time before it was allowed to cool The silica tube was flushed with argon gas for a few seconds before it was lowered into the melt to draw samples The samples were taken both during heating and cooling cycles of the melt. Samples were subjected to sulphur and manganese determination

3.3.3 Melting in Raising Hearth Furnace

Graphite crucible containing metal and additives was covered using a graphite lid It was then placed in another refractory crucible which in turn was covered by a refractory lid The assembly was heated to the desired temperature in the Molybdenum Disilicide furnace and maintained there for certain period of time It was allowed to cool in a pre-determined fashion The crucible was removed from the furnace when the temperature reached 1000°C The solidified metal was recovered by breaking open the graphite crucible and it was subjected to chemical analysis

3.4   Chemical Analysis of the Samples

3.4.1 Sample Preparation

The sample to be analysed was made slag free by grinding etc. It was powdered to size less the 0 15 mm using a pestle and mortar and 100 mesh sieve

3.4.2 Manganese Determation

0.1 g of the powder sample was dissolved in 20 ml of 1 3 nitric acid and boiled for 1 - 2 minutes to expel oxides of nitrogen The solution was then diluted to 60 ml. 5 - 10 ml of syrpury phosphoric acid and 0.5 g of potassium iodate were added. It was then boiled for one minute The solution was cooled and made up to 100 ml. in a volumateric flask. In case where manganese content was more than the instrumental analysis range, necessary dilution was made. The colour of the diluted solution was then matched against

standard samples of known manganese content The wave length of 530 μ was used in the colorimeter analysis The apparatus was calibrated using standard steel samples and cast iron samples of known manganese content.

3.4.3 Sulphur Determination

Sulphur was analysed using H_2S evolution technique in the laboratory The set up was tested for any leakage of gas This was done by pressurising the vessel with argon and noting any pressure drop of argon when supply of argon was cut-off Leak test was also performed in a water tank to see any bubbling due to leakage of gas

For analysing sulphur, 2 5 to 5 g of powdered sample was taken in a conical flask Nearly 60 ml of ammonical $CdCl_2$ was added to the flask The end of the glass tube was kept in this $CdCl_2$ solution 150 ml of 1·1 HCl was poured drop by drop into the conical flask Sulphur in the alloy reacted with HCl to form H_sS gas which was absorbed by ammonical $CdCl_2$ solution to form a yellow precipitate of cadmium sulphide Towards the end of the reaction, heat supply was increased to produce steam and flush out the remaining H_2S in the flask When it was confirmed that the gas has been completely fushed out, the solution was cooled in an ice bath The ice cold solution was acidified with 20 ml of concentrated HCl solution 10 cc of N/30 iodine solution was added to the solution and it was titrated against N/30 $Na_2S_2O_3$ solution using starch as an indicator. It was followed by titration of N/30 iodine solution alone with N/30 $Na_2S_2O_3$. Difference in the two values of $Na_2S_2O_3$ amount is the equivalent amount of $Na_2S_2O_3$ solution consumed for sulphur in the sample The percent sulphur is given by:

$$[\%S] = \frac{0.016 \times 100 \times y}{z \times x}$$

where y is the amount of $Na_2S_2O_3$ consumed, z is the normality of the solution and x is the weight of sample in grams.

Chapter 4

THERMODYNAMIC MODEL FOR Fe-C-Mn-S SYSTEM

4.1 Method for Interpolation of Interaction Parameters

Melting point of iron decreases in presence of carbon It may reach as low as 1150°C at around 4 5 pct Carbon Most of the data for iron alloy are measured at 1600°C with reference to steel making conditions. It is necessary to know values of interaction parameters in the temperature range of 1200 to 1500°C in order to determine sulphur content in the carbon saturated metal Pattjoshi [22] has developed a model for predicting values of interaction parameters by using regular solution model For a regular solution, the quantity $RT \ln \gamma_i$ should not change with temperature. T is temperature in kelvin and γ_I activity coefficient of the solute in the Roultian scale Roultian and Henrian interaction coefficient are defined as follows

$$\varepsilon_i^j = \left(\frac{\partial \left(\ln \gamma_i \right)}{\partial \left(X_i \right)} \right)_{X_i, X_j, X_k \to 0} \tag{4 1}$$

$$\varepsilon_i^j = \left(\frac{\partial \left(\log f_i \right)}{\partial \left(wt \% j \right)} \right)_{wt \% i, j, k \to 0} \tag{4.2}$$

As $RT \ln \gamma_I$ is constant for a regular solution, one can write the following:

$$RT_1\varepsilon_i^j(1) = RT_2\varepsilon_i^j(2)$$

(4 3)

Two types of interaction parameters are related by the following·

$$\varepsilon_i^j = 230\frac{M_j\varepsilon_i^j}{M_1} + \frac{M_1 - M_j}{M_1}$$

(4.4)

where M_j and M_1 are the molecular weight of solute j and solvent iron respectively Let

$$\frac{M_1 - M_j}{M_1} = C_o$$

(4 5)

Combining equations (4.1), (4.4) and (.45) one may obtain the following.

$$\frac{1 - \left(\dfrac{C_o}{e_i^j(1)}\right)}{1 - \left[\dfrac{T_2 C_o}{T_1 e_i^j(1)}\right]} = \frac{T_1 e_i^j(1)}{T_2 e_i^j(2)}$$

(4.6)

By knowing the value of $e_i^j(1)$ at temperature T_1, are can calculate value of e_i^j at any other temperature T_2.

4.2 Thermodynamic Model

The various incoming and outgoing species are listed in Table 4 1 for the development of model equations

The following assumptions are made:

1   Added amounts of iron sulphide and manganese dissolve completely in iron alloy

2   Sulphur in the metal goes to the slag either as MnS or FeS

3   The equilibrium exits between slag and metal at the reaction temperature

4. The standard state for sulphur is taken as $S_{(4\,35\%C)}$.

5   Elements such a silicon, phosphorous and carbon do not form any reaction products

6. Weight fraction of FeS and MnS are equal to their mole fraction

7   MnS and FeS in the slag form an ideal solution

Sulphur balance for the system gives the following equation:

$$Y_1 = \left[\frac{32.0 \times W_{FeS}/88.0 + 0.01 \times (X_S \times W_{hm} - Y_2 \times Y_5)}{1 - Y_3/88} \right] \frac{87}{32}$$ (4.7)

Overall balance of the metal phase given the following

$$Y_2 = W_{hm} + W_{FeS} + W_{Mn} - Y_1$$ (4.8)

Manganese balance yields the following

$$Y_7 = 100 \left(\frac{\left(W_{hm} \cdot X_{Mn} 0.01 + W_{Mn}\right)(100 - 0.61 Y_1 Y_4)}{Y_2} \right)$$ (4 9)

Slag-metal equilibrium may be represented by the followings:

$$[Fe] + [S] = (FeS)_{slag}$$ (4.10)

Table 4 1   Lists of symbols used for material balance

Input

W_{FeS}	-	weight of FeS added
W_{Mn}	=	amount of Mn added
X_C	=	percentage of C in hot metal
X_{Si}	=	percentage of Si in hot metal
X_S	=	percentage sulphur in hot metal
X_P	=	percentage of P in hot metal
X_{Mn}	-	percentage of Mn in hot metal
X_{fe}		percentage of Fe in hot metal
W_{hm}	-	amount of metal

Output

Y_1	-	amount of slag
Y_2	-	amount of metal
Y_3	-	weight fraction of FeS in the slag
Y_4	=	weight fraction of MnS in slag
Y_5	-	percentage of S in hot metal
Y_6		percentage of Si in hot metal
Y_7		percentage of Mn in hot metal
Y_8	-	percentage of P in hot metal
Y_9	=	percentage of Fe in hot metal
Y_{10}	=	carbon pick up.

$$\Delta G^{o} = -6090\,0 + 4\,03\,T \tag{4 11}$$

$$k_{FeS} - \frac{Y_{3}}{f_{s}Y_{4}} \tag{4 12}$$

$$[Mn] + [S] = (MnS) \tag{4 13}$$

$$\Delta G^{o} = -39220\,0 + 20\,87\,T \tag{4 14}$$

$$k_{MnS} \quad \frac{Y_{4}}{Y_{7}Y_{5}f_{s}f_{Mn}} \tag{4 15}$$

f_s and f_{Mn} in equations 4 12 and 4 15 respectively are calculated from the following equations

$$\log f_{s} - \sum_{i\,1}^{N} e_{s}^{j}(wt.\%\,j) \tag{4.16}$$

$$\log f_{Mn} - \sum_{i\,1}^{N} e_{s}^{j}(wt\,\%\,j) \tag{4.17}$$

Here j stands for solute elements like C, Mn, S, P, Si. The value of e_{s}^{j} at different temperature can be calculated from the interpolating method given in Section 6. Computer programme was developed to solve the model equations. Details of the programme are given in the Appendix. Results of calculations are plotted to Figs 4.1
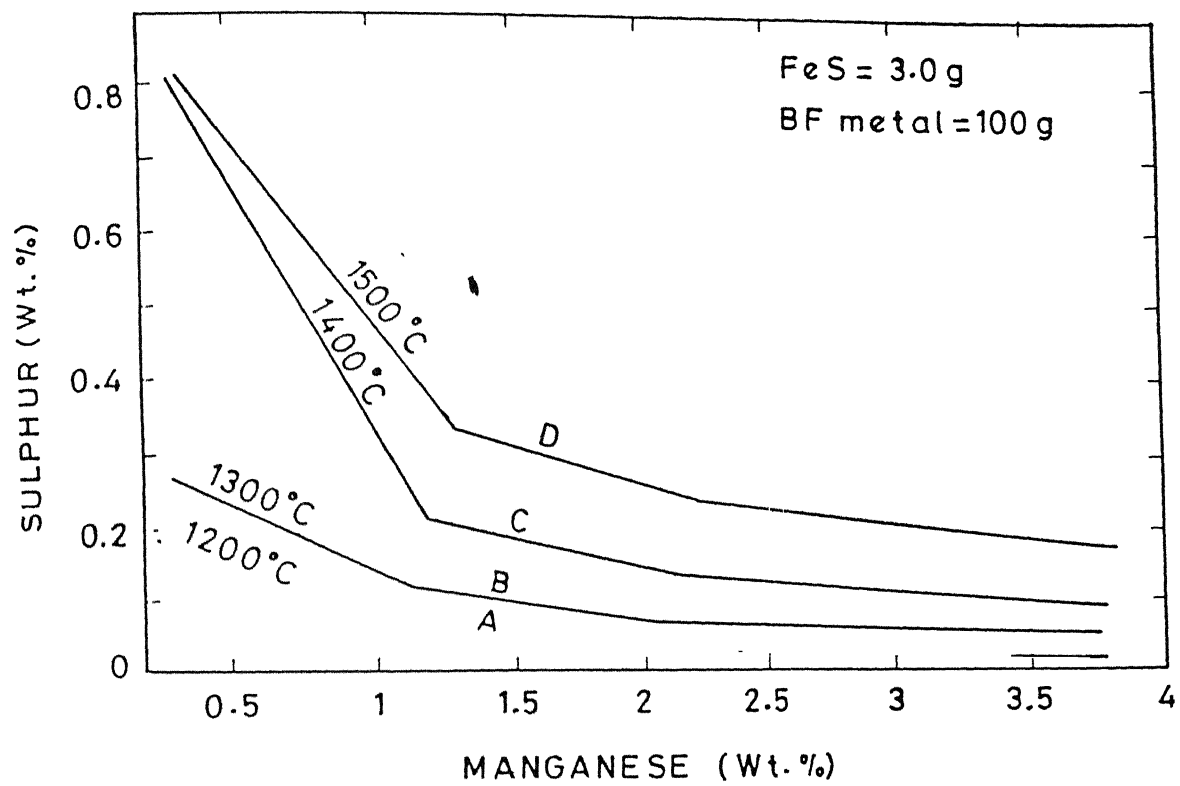
Figure 4.1: plot to show effect of manganese on calculated value of sulphur at different temperature.

CHAPTER 5

RESULTS AND DISCUSSION

Details of experiments carried out in the present study are included in Table 5 1 For experiments in category A and C, crucibles containing the required amount of metal and additives were slowly heated and held in the raising hearth furnace for 6h and 2h respectively at 1500°C and then allowed to cool in the furnace itself For experiments in category B, thermal cycle consisted of the following

1   Heating the crucible in the furnace to 1500°C and holding there for 90 minutes

2   Cooling the crucible in the furnace to 1400°Cand holding there for 120 minutes

3.   Cooling the crucible in the furnace to room temperature

Experiments in category D and E were conducted in the silicon carbide furnace. Crucible containing the metal and additives was heated to the temperature beyond the melting range of the alloy and then allowed to cool in the furnace till the liquid metal resolidified Samples were drawn from the melt at different temperatures both during heating and cooling cycles

Results of sulphur determination in samples obtained from different experiments are summarised in Table 5.2. Sulphur contents of the standard sample was determined a number of times to check the reliability of the apparatus and the method used to analyse sulphur content of the metal. Results are summrised in the Table 5 3 Determination of the sulphur content in the metal may be considered reliable because of the good agreement obtained between the experimentally determined values and the reported values for the standard sample. Experimentally determined manganese contents in these samples are plotted against estimated values in Fig 5.1. Because of the uncertainty in the analysis of manganese in metal samples in some experiments, manganese content of the sample was estimated by making the manganese balance
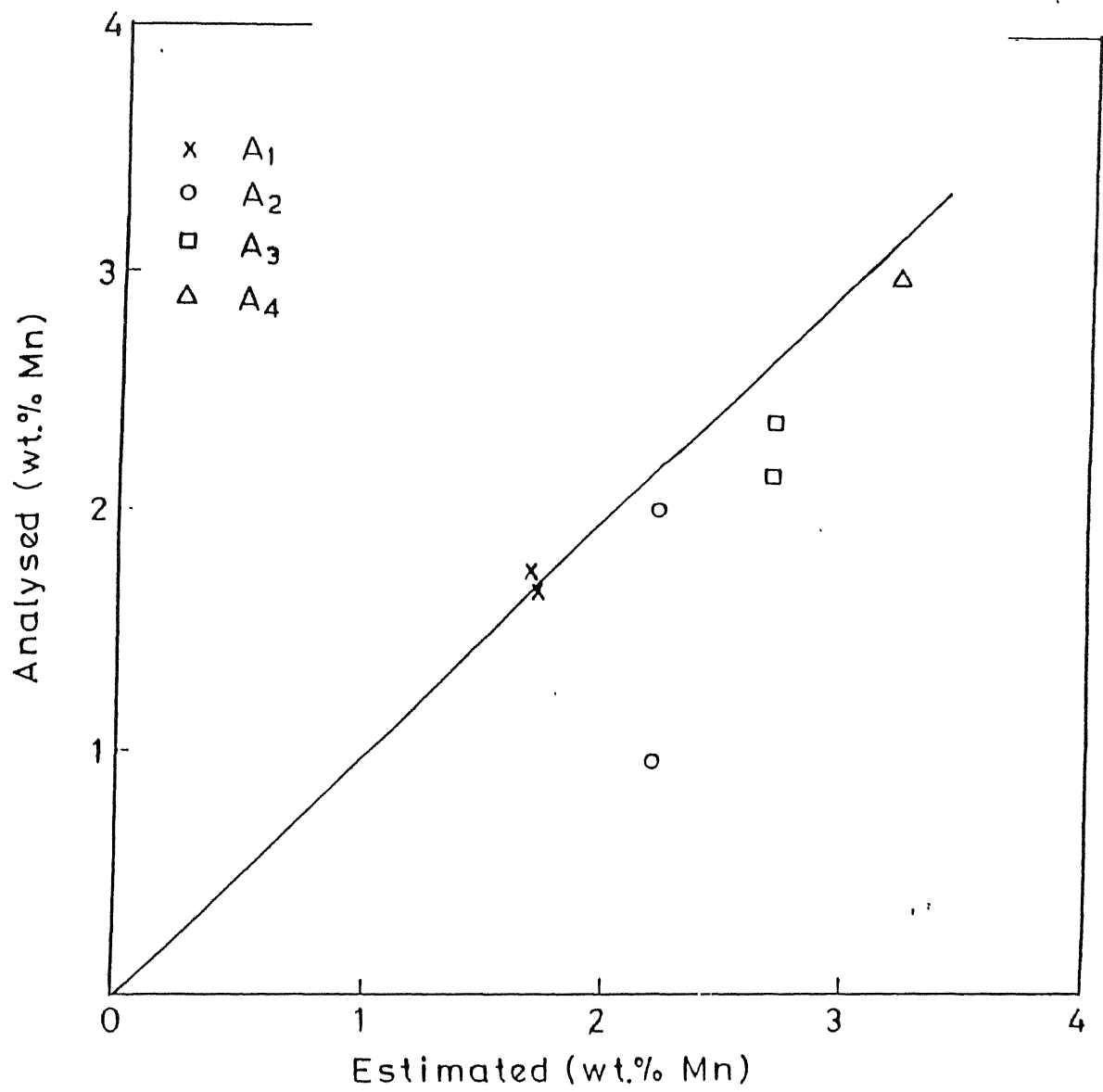
Figure 5.1 Analyzed manganese content of metal phase versus estimated

manganese content for A category of experiments

For all experiments it was ensured that there was practically no slag adhering to metal sample before doing any analysis It was possible to obtain slag free metal samples in a silica tube in experiments D_1 to D_3 For runs A_1 to A_4 and B_1 to B_3, slag free samples for analysis could be obtained by grinding the slag off the solidified metal For runs C_1 to C_3, solidified slag layer was first removed by repeated hammering after breaking out the crucible Clean and slag free metal for chemical analysis was obtained by further grinding off slag. For runs E_1 to E_3, enough care was taken to draw slag free samples from the liquid metal pool by ensuring that the end of the silica tube was beneath the slag level in the crucible These samples were further machined using a grinder to make them completely free of any adhering slag layer

Results show that for the experiment A_1 to A_4 and B_1 to B_3, sulphur content of metal decreased as manganese content increased Results are plotted in Fig 5.2 and compared with theoretical predictions at different temperatures using model equations described in chapter 4 Measured sulphur contents are much less than the predicted values at 1500°C However, measured values match well with the predicted values in the temperature range of 1200 -1300°C One may conclude that there occurred a drop in sulphur during cooling of metal. As it took more than two hours for the liquid metal to solidify when left alone in the furnace, manganese could combine with sulphur to form manganese sulfide This explains the results of most of experiments in category A and B Limited number of experiments in category C on slag metal equilibrium highlight the following:

1   Sulphur content decreases with an increase in slag basicity i e CaO/SiO_2 ratio.

2   Sulphur content of metal is lowered by increasing the slag volume

From sulphur balance, one may show that sulphur content of metal is related to sulphur partition ratio as follows·
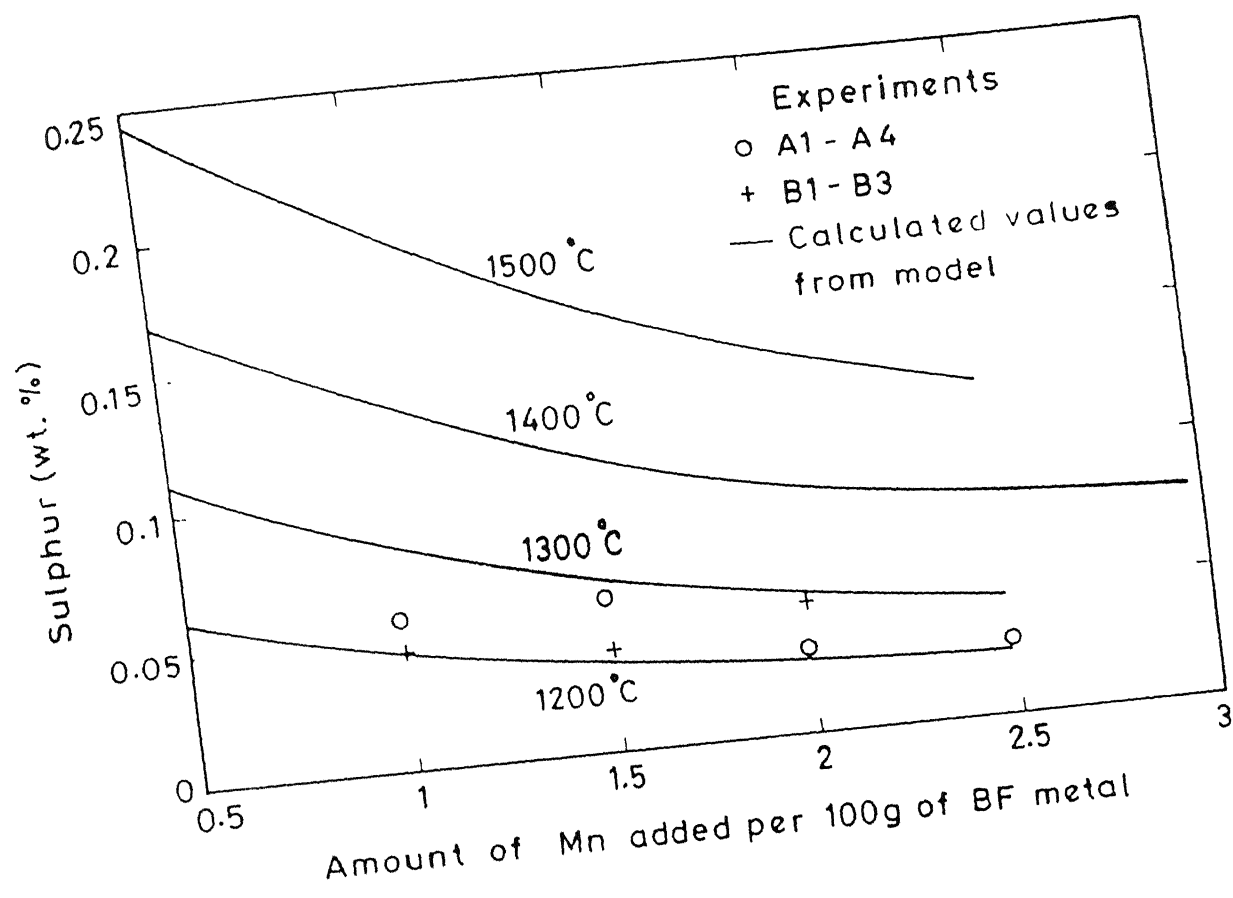
Figure 5.2: Plot to show change in sulphur content with manganese addition

$$[S] = \frac{(3200/88) \ (W_{FeS}/W_{BF}) + 0\,04}{\alpha \ (W_{slag}/W_{BF}) + 1}$$

Sulphur content of blast furnace metal has been taken as 0 04 pct From the results of experiment, calculated values of the sulphur partition ratio can be obtained and these are summarized in Table 5 4 Higher values of the sulphur partition ratio obtained at lower lime to silica ratio in experiment C_3 may be attributed to kinetic factors Time taken by the metal to cool from 1500 to 1200°C is an important factor in presence of the manganese in such experiments It confirms that both thermodynamic and kinetic factors are important to study to explain desulphurization of metal For experiments D_1 and D_2, experimentally determined values and the values determined by using the model equations are plotted against temperature in Fig 5 3 There is good agreement between the two sets of sulphur contents of the metal Results of experiment D_3 are also found to match well with the predicted values For experiments E_1 and E_2, sulphur contents of the metal are compared with the predicted values from the model in Fig 5.4. Sulphur contents of the metal are found to be lie in the range which is based on manganese sulphur equilibrium in the melt This may be attributed to the fact that the slag was not playing any effective role in desulphurization as there was no stirring in the melt
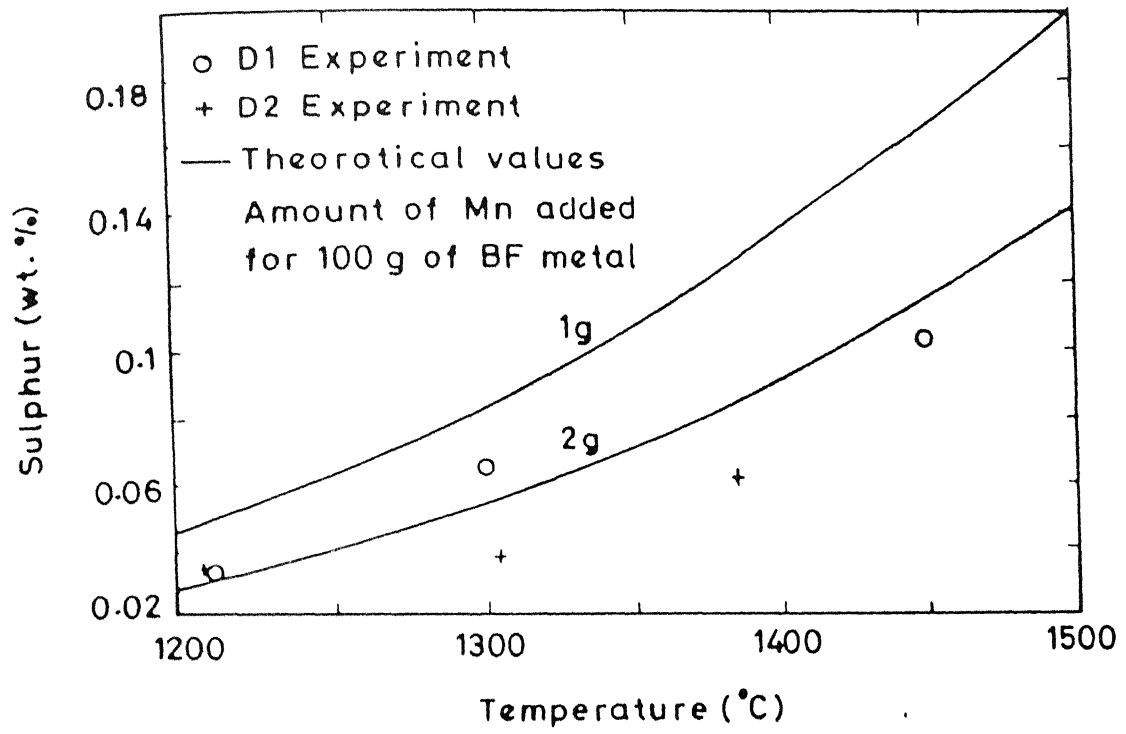
Figure 5.3: Plot to show change in equilibrium value of sulphur in the melt with temperature.
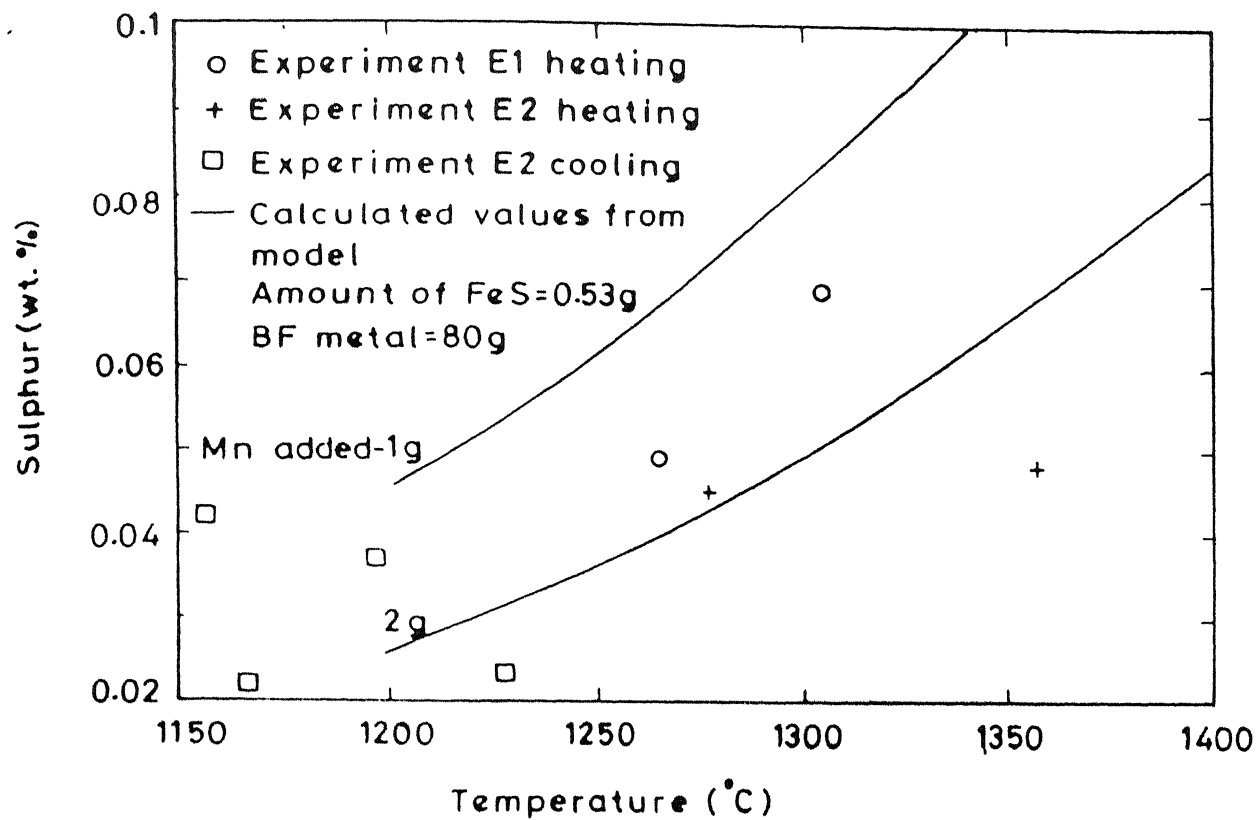
Figure 5.4 Plot to compare the sulphur content of the melt in experiments E1 and E2 with the value predicted by the model

TABLE 5.1

Details of Experiments Carried out in the Present work

Category	S N	BF Metal	FeS	Mn	CaO	Al$_2$O$_3$	SiO$_2$	Master Slag
		g	g	g	g	g	g	g
A	A$_1$	100	0 277	1 043	-	-	-	-
A	A$_2$	100	0 277	1 543	-	-	-	-
A	A$_3$	100	0 277	2 001	-	-	-	-
A	A$_4$	100	0 277	2.501	-	-	-	-
B	B$_1$	100	0 277	1 049	-	-	-	-
B	B$_2$	100	0 277	1 504	-	-	-	-
B	B$_3$	100	0 277	2.014	-	-	-	-
C	C$_1$	83	0 277	0	16	8	16	-
C	C$_2$	83	0 277	0	17 5	8	14 5	-
C	C$_3$	83	0 277	0	26.2	8	35 5	-
D	D$_1$	100	0 377	1.005	-	-	-	-
D	D$_2$	100	0 377	2 009	-	-	-	-
D	D$_3$	100	0 754	6.009	-	-	-	-
E	E$_1$	80	0.554	1	-	-	-	24
E	E$_2$	80	0.554	2	4	-	-	20

TABLE 5.2

Results of Sulphur Determination in Metal Samples Collected

Experiment No	Temperature of Taking Sample oC	Sulphur Content I %	Sulphur Content II %	Sulphur Content (average) %
A_1	*	0 058	-	0 058
A_2	*	0 059	-	0.059
A_3	*	0.034	-	0.034
A_4	*	0 030	-	0 030
B_1	*	0 045	-	0.045
B_2	*	0 039	-	0 039
B_3	*	0.050	-	0 050
C_1	*	0 042	0 034	0.037
C_2	*	0.035	0 030	0 033
C_3	*	0 0168	0.0163	0.0165
D_1	1212	0 034	-	0 034
D_1	1301	0 065	0 073	0 069
D_1	1450	0.104	-	0 104
D_1	*	0.0448	-	0 0448
D_2	1208	0.035	-	0.035
D_2	1304	0 035	0 041	0 038
D_2	1385	0 062	-	0.062
D_1	1212	0.034	-	0.034
D_1	1301	0.065	0.073	0.069
D_1	1450	0.104	-	0 104

Table 5.2 Continued

D$_2$	1208	0.035	-	0.035
D$_2$	1304	0.035	0 041	0 038
D$_2$	1385	0.062	-	0.062
D$_2$	*	0 040	-	0.040
D$_3$	1250	0.0362	-	0.0362
D$_3$	1300	0.0373	-	0.0373
D$_3$	1350	0.049	-	0.049
D$_3$	*	0 033	-	0.033
E$_1$	1265	0.049	-	0.049
E$_1$	1305	0.069	-	0.069
E$_1$	*	0.0560	-	0.056
E$_2$	1277	0.0448	-	0.0448
E$_2$	1357	0.048	-	0.048
E$_2$	1227	0.023	-	0.023
E$_2$	1197	0.037	-	0.037
E$_2$	1167	0 022	-	0.022
E$_2$	1157	0.042	-	0 042

* Solidified metal in the crucible after the experiment.

TABLE 5.3
Results of Analysis of Standard Cat Iron Sample

S.N.	Sulphur %
1	0.0533
2	0 0629
3	0.052
4	0.0607
5	0.062
6	0.064
Average	0.059
Reported	0.067

TABLE 5.4

Results of Calculations of Sulphur Partition Ratio

Experiment No	CaO/SiO$_2$ ratio	W$_{FeS}$/W$_{BF}$ Ratio	S$_{slag}$/W$_{BF}$ Ratio	Sulphur Content %	Partition Ratio
C1	1 0	0 00335	0 48	0 027	4 8
C2	1 2	0 00335	0 48	0 035	5 2
C2	1 20	0.00335	0 48	0 030	6 4
C3	0 73	0 00335	0 94	0 0163	6 9
C3	0 73	0 00335	0 94	0 0168	6 6

CHAPTER 6

SUMMARY AND CONCLUSION

(1) Model equations based on materials balance and slag metal equilibrium have been developed and solved using a computer programme to determine sulphur content of the metal phase due to additions of different proportions of iron sulphide and manganese metal to blast furnace iron at different temperatures of the bath

(2) Results of model calculations show that sulphur content of metal decreases with an increase in manganese content of the bath at constant temperature Results also reveal that sulphur content tends to fall with lowering of metal temperature at constant manganese content of the metal.

(3) One silicon carbide tube furnace has been designed and constructed in the laboratory to reach $1400^{\circ}C$ Its temperature can be controlled within $\pm 2^{\circ}C$ Samples of bath can be drawn during heating and cooling stages Results of sulphur analysis of the samples agreed well with the predicted results using the model equations

(4) Some experiments were carried out by addition of manganese as well as slag but without any stirring of the bath. Results showed that sulphur content did not fall beyond the levels predicted by the manganese sulphur interactions.

(5) Some experiments were carried out using the raising hearth type furnace at 1400 and $1500^{\circ}C$. Samples could not be taken during the experiment duration Sulphur content of the solidified metal in the crucible after the experiment agreed with the model results at 1200 and $1300^{\circ}C$ and not at 1400 and $1500^{\circ}C$ It shows that considerable drop in sulphur occurred during cooling stages even without stirring of the bath

(6)   Practical importance of the study lies in the observed drop in sulphur content of hot metal in the ladle during its transport from the blast furnace to mixer stage in the steelmaking shop whenever the manganese content of metal exceeded 1 pct Further drop in sulphur may be envisaged if slag is added to decrease the activity of manganese sulphide but this may require extensive stirring of the bath

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COMPUTER PROGRAMME TO SOLVE MODEL EQUATIONS IN Fe-C-Mn-S SYSTEM

```
      real k1,k2,wfes,xc,xsi,xs,xmn,t,r,eps,yfes,ymns,yfe,yc,ycc,whm
      real ycpick,ycl,tl,ar,br,a,b,fs,fmn,at,fein,feout,ymetal
      real wmn,xfe,yslag,tc,ymn,ysi,yp,error,yss,xp,ys
      open(20,file='in.dat')
      open(21,file='out1.dat')
      open(22,file='out2.dat')
      wfes=0.5535
      whm=80.
      wmn=2.0
       xc=4.3
       xsi=0.5
       xs=0.05
       xp=0.25
       xmn=0.7
       t=1200
       r=1.987
       eps=0.001
      read(20,*) wfes,whm,wmn,xc,xsi,xs,xp,xmn,t,r,eps
      write(22,223)
223   format(25x,'%C     %Si    %P      %Mn     %S    Temp. C error'//)
      write(21,225)
225   format(25x,'metal    slag    Fes     Mns'//)
      do i=1,7
      t=1200+50*(i-1)
       xfe=100.-xc-xsi-xp-xmn-xs
       tl=t+273.
       a=((-31580.0/(r*tl))+19.61/r)
       k1=exp(-a)
       b=((1550.0/(r*tl))+2.63/r)
       k2=exp(-b)
       ar=1.34+2.54*0.001*t
       br=0.04*xmn-0.35*xp-0.4*xs-0.3*xs
       ycl=ar+br
       yc=ycl
       ys=xs
       ymetal=whm+wfes+wmn
       fs=7.0
       fmn=0.8
102    ycpick=(ymetal*yc-xc*whm)*0.01
101    yfes=ys*k2*fs
       if(yfes.le.1.0) go to 222
       yfes=1.0
       ys=1.0/(k2*fs)
222    ymns=1-yfes
       at=(32.0*wfes/88.0+0.01*(xs*whm-ymetal*ys))*(87./32.)
       yslag=at/(1.0-0.0042*yfes)
       ymn=100.*(wmn+0.01*xmn*whm-(55./87.)*ymns*yslag)
        /ymetal
       yss=ymns/(ymn*k1*fmn*fs)
       if(abs(yss-ys).le.eps)goto 100
       ys=yss
       goto101
100     ys=yss
       ysi=(xsi*whm)/ymetal
       yp=(xp*whm)/ymetal
       tc=0.04*ymn-0.35*yp-0.4*ys-0.3*ysi
```

```fortran
          ycc=ar+tc
          if(abs(ycc-yc).le.0.001)goto 106
          yc=ycc
          goto 102
106       yc=ycc
          ymetal=whm+wmn+wfes+ycpick-yslag
          fein=(56.*wfes)/88.+0.01*xfe*whm
          yfe=100.-ymn-ysi-yp-yc
          feout=0.01*ymetal*yfe+yslag*yfes*0.636
          error=(feout-fein)*100.0/fein
c         print *,ymn,yfe,ymns,yfes,yslag,ys,ymetal
          write(21,221)ymetal,yslag,yfes,ymns
          write(22,224)yc,ysi,yp,ymn,ys,t,error
221       format(/22x,4f7.2)
224       format(/22x,5f7.3,f7.1,f7.3)
          enddo
          stop
          end
```
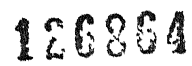
```fortran
                    ycc=ar+tc
                    if(abs(ycc-yc).le.0.001)goto 106
                    yc=ycc
                    goto 102
106                 yc=ycc
                    ymetal=whm+wmn+wfes+ycpick-yslag
                    fein=(56.*wfes)/88.+0.01*xfe*whm
                    yfe=100.-ymn-ysi-yp-yc
                    feout=0.01*ymetal*yfe+yslag*yfes*0.636
                    error=(feout-fein)*100.0/fein
c                   print *,ymn,yfe,ymns,yfes,yslag,ys,ymetal
                    write(21,221)ymetal,yslag,yfes,ymns
                    write(22,224)yc,ysi,yp,ymn,ys,t,error
221                 format(/22x,4f7.2)
224                 format(/22x,5f7.3,f7.1,f7.3)
                    enddo
                    stop
                    end
```

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